

Lectures
on
Theoretical and Physical
Chemistry

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PART II
CHEMICAL STATICS

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PREFACE

THE following work on Chemical Statics reproduces the lectures given by me in the winter and summer semesters, 1897-98, at the University of Berlin, under the title 'Selected Chapters in Physical Chemistry.' It is a second part to the 'Chemical Dynamics,' but at the same time is as far independent as possible, and deals with the methods which yield conclusions as to molecular magnitude, structure, and grouping, and consequently bring into life our present conceptions on the structure of matter. The theory of solutions and stereochemistry are treated especially fully, in accordance with the present interest attaching to them. That Part I of the 'Lectures on Theoretical and Physical Chemistry' has already been translated into French and English may perhaps be regarded as a recommendation of the present Second Part.

J. H. VAN 'T HOFF.

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CONTENTS OF PART II



THE DIVISION OF THE WORK AND THE TREATMENT CHOSEN	PAGE 9
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PART II. CHEMICAL STATICS.

CONTENTS AND ARRANGEMENT	11
The atomic hypothesis	11
The molecular hypothesis	13
<i>I. MOLECULAR WEIGHT AND POLYMERISM.</i>	
Molecular weight determinations by chemical methods . . .	15
Physical methods for determination of molecular weight . .	16
§ 1. MOLECULAR WEIGHT DETERMINATION IN DILUTE	
GASES	16
A. Avogadro's law	16
B. Methods for molecular weight determination in gases . .	19
1. Ordinary process	19
2. Determination of vapour density by means of the second law of thermo-dynamics	20
C. Results	22
1. Connexion with the atomistic hypothesis	22
2. Confirmation and testing of atomic weights	23
3. Nature of the elementary molecules, and polymerism . .	24
Polyatomicity. Hydrogen	24
Monatomic elements. Mercury	25
Allotropy of the elements. Ozone and oxygen	26
Dissociation of the elements at high temperature. The halogens	26
Polymerism	27

	PAGE
§ 2. MOLECULAR WEIGHT DETERMINATION IN DILUTE SOLUTIONS	27
A. The theory of dilute solutions	28
1. Henry's law and the constitution of the dissolved gas	28
2. Avogadro's law for dissolved substances	31
B. Methods for molecular weight determination of dissolved bodies	36
1. Direct methods for molecular weight determination of dissolved bodies	36
(a) Comparison of the osmotic pressure of different solutions (Isotony)	36
(b) Absolute measurement of osmotic pressure	39
2. Indirect methods for molecular weight determination	41
(a) The cyclic process can be carried out at constant temperature	42
Molecular weight determination by vapour pressure measurement	42
Deduction of the law of diminution of vapour pressure without thermo-dynamics	43
Thermo-dynamic deduction of the law of diminution of vapour pressure	46
Abnormal values for abnormal vapour densities	47
Accuracy attainable in measuring vapour pressures	49
Molecular weight determination by lowering of solubility	50
Ratio of partition	53
(b) The cyclic process cannot be carried out at constant temperature	54
Molecular weight determination by lowering of the freezing point	54
Molecular weight determination by the rise of boiling point	57
Molecular weight determination by means of the change of solubility with temperature	58
C. Results	59
1. Simple molecular magnitude of dissolved bodies	59
Larger molecules. Agreement with the results of gas density measurements	59
Larger molecules in hydroxylic compounds	60
2. Development of the stereochemical conceptions	61
3. Abnormal results for isomorphous compounds	61
4. Abnormal results for electrolytes	62
The theory of electrolytic dissociation	62
Electrolytes which follow Ostwald's law of dilution	66
Electrolytes which do not follow Ostwald's law of dilution	67

CONTENTS

7

	PAGE
§ 3. SOLID SOLUTIONS	70
A. Qualitative considerations	70
B. Quantitative results	72
1. Isomorphous mixtures of electrolytes	73
2. Crystalline mixtures of non-electrolytes	74
Crystalline solid solutions	75
Isomorphous mixtures	76
3. Amorphous solid solutions	77
II. MOLECULAR STRUCTURE (<i>Isomerism, Tautomerism</i>).	
§ 1. DETERMINATION OF CONSTITUTION	83
A. Determination of constitution on the basis of the valency of the elements combined	83
B. Determination of constitution from formation out of, and conversion into compounds of known structure	83
Intramolecular atomic displacements	88
§ 2. DETERMINATION OF CONFIGURATION (Stereochemistry)	90
A. Determination of configuration by the number of isomeric derivatives	91
1. Constitution of benzene	91
(a) Benzene gives only a single monosubstituted derivative	92
(b) Existence of only three bisubstituted derivatives	94
(c) Benzene substitution products not optically active	94
2. Determination of position in the benzene derivatives	97
B. Determination of relative distances in the molecule	98
1. Mutual action of different groups	98
2. Mutual influence of different groups	100
C. Stereochemistry	102
1. The asymmetric carbon atom and separation into optical antipodes	104
(a) Methods based on the phenomena of solution	107
(a) Spontaneous separation	107
(b) Separation by forming salts with active acids and bases	114
(b) Methods of separation depending on chemical action. Separation by means of enzymes and organisms	115
2. Simple carbon linkages and compounds with more than one asymmetric carbon atom	116
The principle of free rotation	116
Number of isomers in multiple asymmetry	117
Inactive undecomposable type	118
Several asymmetric carbon atoms	119

3. Double linkage and ring formation	120
Carbon double linkage	121
Ring formation	124
4. Stereochemistry of other elements	124
Concluding remark on stereochemistry	125
§ 3. TAUTOMERISM	126

III. MOLECULAR GROUPING (*Polymorphism*).

§ 1. LAWS REGULATING THE MUTUAL CONVERSION OF POLYMORPHIC SUBSTANCES	133
A. The stable modification must have the smaller vapour pressure and the smaller solubility	134
B. The stable modification must have the higher melting point	134
C. Possibility of a transition temperature	135
D. When there is a transition temperature, the modifica- tion stable at low temperatures is formed from the other with evolution of heat	136
E. Polymorphic modifications have a constant ratio of solubilities, proportional to the differential coeffi- cients of the saturation pressures, in solvents which take up so little of the substance, that the laws of dilute solutions are applicable	137
§ 2. ACTUAL MOLECULAR ARRANGEMENTS	140
A. Relative position of molecule centres in the crystalline figure	140
1. The fundamental law of geometrical crystallography (F. C. Neumann)	140
2. Attempt at explanation of the geometrical law by arrange- ment of molecule centres (Frankenheim, Bravais)	141
3. Relations of symmetry in crystals	141
4. Sohncke's point systems	141
5. The fundamental law of physical crystallography	141
6. Molecular compounds	141
B. Orientation of the molecules in the crystal	142
1. Relations between symmetry in the crystal and in the molecule	142
2. Influence of changes in the molecule on the crystalline form	142

THE DIVISION OF THE WORK AND THE TREATMENT CHOSEN

In the inevitably arbitrary division of any subject it is well to choose so that it may easily be seen where each part belongs. For this reason the treatment adopted by Lothar Meyer in the later editions of his *Modern Theories of Chemistry* seemed to me appropriate for my lectures: in it the whole is divided into Statics and Dynamics. Statics then deals with single substances, i.e. with views on the structure of matter, the conception of atoms and molecules, and on constitution so far as the determining of molecular configuration. Dynamics is devoted to the mutual actions of several substances, i.e. to chemical change, affinity, velocity of reaction, and chemical equilibrium.

To these I have added a third section, in which the chief object is the comparison of one substance with another, and consequently the relations between properties—both chemical and physical—and composition.

In preparing for the press I have preserved this arrangement, only making a change in the order in accordance with the development of chemical science in the last ten years. Until then Dynamics, that is the study of reactions and of equilibrium, took a secondary place. But lately, and especially since the study of chemical equilibrium has been related to thermo-dynamics, and so has steadily gained a broader and safer foundation, it has come into the foreground of the chemical system, and seems more and more to belong there.

The following arrangement is therefore chosen as an experiment:—

First Part: Chemical Dynamics.

Second Part: Chemical Statics.

Third Part: Relations between Properties and Constitution.

The logical advantage gained in this way is essentially that in the First Part it is possible to proceed without any hypothesis on the nature of matter, only the molecular conception being made use of. Not till the Second Part does the atomic hypothesis come to the front, and with it problems of configuration. Finally comes the still very obscure problem of the relation of one body to another.

There are two points, however, that should be referred to. From the logical side it may be objected that Statics is concerned with the simpler problem, since it deals with single substances at rest, whereas Dynamics deals with a complex of substances in action. This objection, however, has less force when one remembers that the single substance corresponds to the state of equilibrium following a completed reaction—and indeed the simplest form of equilibrium—and accordingly Part II is devoted to the more detailed study of this final state.

From the pedagogic point of view, placing Dynamics first can be dubious only to those chemists who are not well prepared in Physics, and consequently have not mastery over the chief lines of their own subject.

The treatment chosen corresponds with that I have followed in teaching. It consists essentially in developing each generalization from a specially chosen concrete experimental case. On this follow an exhibition—as far as possible graphic—of the leading results, the conclusions drawn, and, lastly, theoretical remarks on the generality and applicability of the conclusions.

PART II

CHEMICAL STATICS

Contents and arrangement. As explained in the introduction, chemical statics treats a single substance as a case of equilibrium of the simplest kind, occurring on completion of a reaction. It is, in the first instance, defined by its qualitative and quantitative composition. But as, for the same composition, it is possible to have different states of equilibrium, e.g. polymerism and isomerism, a closer characterization is necessary. The external features, apart from hypothesis, whether physical, such as heat of formation, density, optical rotation, crystalline form, and so on, or chemical, as affinity, velocity of reaction, and so on, have not up to the present afforded any means of predicting the conditions of such polymerism or isomerism. The case is different if molecular and atomistic theory be taken as the starting point. We must therefore treat chemical statics in this sense too, i.e. we must develop the views as to the internal structure of matter, after saying a word on the basis of the molecular and atomistic treatment.

The atomic hypothesis, it is well known, is an attempt at explaining the peculiar relationships observed in the quantitative composition of compounds. Three fundamental laws have proved to be strictly true:—

1. The law of constant composition, which amounts to saying that a compound, however prepared, has always

the same composition, e. g. silver chloride always contains 75.26 % Ag.

2. The law of multiple proportions, according to which two elements that come together in several compounds occur in the same ratio, or in ratios that are related by means of whole numbers; e. g. compare

Silver chloride (with 24.74 % Cl and 75.26 % Ag) and

Silver chlorate (with 18.54 % Cl and 56.40 % Ag);

the ratio of chlorine to silver is the same in the two, viz.:

$$24.74 : 75.26 = 0.329 \text{ and } 18.54 : 56.40 = 0.329.$$

On the other hand, compare

Chlorine iodide (21.84 % Cl and 78.16 % iodine) and

Chlorine tri-iodide (8.52 % Cl and 91.48 % iodine);

the two ratios of chlorine to iodine are in a whole number proportion, for

$$21.84 : 78.16 = 0.279 \text{ and } 8.52 : 91.48 = 0.093 = \frac{1}{3} \times 0.279.$$

3. The law of equivalents, which expresses that two elements combine with equal quantities of a third, in a ratio equal to that in which they combine with one another, or in a ratio related to the latter by a whole number. If, e. g., we compare

Silver chloride (24.74 % Cl and 75.26 % Ag),

Silver iodide (54.04 % I and 45.96 % Ag), with

Chlorine iodide (21.84 % Cl and 78.16 % I),

the ratio of the amounts of the elements combined with equal amounts—say 75.26 parts—of silver is:

$$24.74 : 54.04 \times \frac{75.26}{45.96} = 0.279,$$

i. e. the same as in the direct combination of chlorine and iodine.

If we had chosen chlorine tri-iodide (with ratio 0.093) as instance, then obviously the integral ratio 3:1 would have been found.

These three fundamental laws are explained on the atomistic hypothesis. Assuming that the elements chlorine, silver, and iodine occur in discrete particles of fixed mass—atoms (chlorine = $\text{Cl} = 35.5$, silver = $\text{Ag} = 108$, iodine = $\text{I} = 127$)—we have:—

1. In the symbol AgCl for the particles of which silver chloride consists, the expression for its constant composition.

2. In the symbol AgClO_3 for silver chlorate the expression that here chlorine and silver combine in the same proportion as in silver chloride; whilst the formulae ICl and ICl_3 or generally I_mCl_n and I_pCl_q refer directly to the integral relation between the proportions in which iodine and chlorine occur in the later example:

$$\frac{m\text{I}}{n\text{Cl}} : \frac{p\text{I}}{q\text{Cl}} = \frac{m}{n} : \frac{p}{q} = mq : np.$$

3. The constant or multiple ratio of combination between chlorine and iodine indirectly (combined with equal amounts of silver) and directly is equally expressed by the three general symbols



since the ratios of the halogens combined with the same amount of silver and the direct ratio of combination are given by

$$\frac{q\text{Cl}}{p\text{Ag}} : \frac{s\text{I}}{r\text{Ag}} = \frac{qr\text{Cl}}{ps\text{I}} \text{ and } \frac{n\text{Cl}}{m\text{I}},$$

whilst

$$\frac{qr\text{Cl}}{ps\text{I}} : \frac{n\text{Cl}}{m\text{I}} = qrm : psn.$$

It may be added that the assumption of the invariability of these atoms in quantity and quality is a simple expression of the empirical law of the conservation of mass and of the invariability of the elements.

The molecular hypothesis is a direct consequence of the assumption of atoms, and so rests also on a chemical basis.

It is very important, however, that it was developed independently in the region of physics, and that the relations between molecular weights so formed could be brought into perfect harmony with those obtained on chemical grounds.

Starting from these hypotheses on the nature of matter, and bearing in view the aim of explaining differences of properties when the qualitative and quantitative composition is the same, we have first to consider molecular weight, and the special kind of isomerism that is referred to differences of molecular weight, i.e. polymerism. Next comes the internal structure of the molecule, with the differences so arising, and associated with the phenomenon of isomerism in the narrower sense. Finally comes the arrangement of molecules to form crystalline figures whose differences constitute the phenomenon of polymorphism or physical isomerism. Accordingly the following division is adopted:—

- I. Molecular weight and polymerism.
- II. Molecular structure and isomerism.
- III. Molecular grouping and polymorphism.

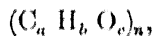
I. MOLECULAR WEIGHT AND POLYMERISM

As mentioned above, the molecular hypothesis rests upon a basis both chemical and physical. Accordingly the methods for the determination of molecular weight belong partly to chemistry, partly to physics.

Molecular weight determinations by chemical methods start from the atomistic hypothesis, according to which the molecule is built up of atoms; e. g. if a compound contain p , q , and r per cent. of carbon ($C=12$), hydrogen ($H=1$), and oxygen ($O=16$) respectively, the ratio of the number of atoms a , b , and c is given by

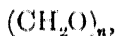
$$a : b : c = \frac{p}{12} : q : \frac{r}{16},$$

in which a , b , and c must be whole numbers. This does not, however, allow of fixing a , b , and c , for if the least integral relation has been calculated all the formulae



in which n is unity, or some other integer, would satisfy the conditions.

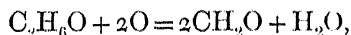
To determine n therefore requires a second criterion, which in the region of chemistry mostly leads with sufficient probability to a decision, but so far not with absolute certainty. It is supplied by the chemical behaviour—combination and reaction—which renders certain molecular weights probable. Thus taking acetic acid



and remembering that it arises by oxidation of alcohol, for which the simplest possible formula is C_2H_6O , and forms

a silver salt $C_2H_3AgO_2$ containing at least two carbon atoms in the molecule, $n=1$ for acetic acid is practically excluded, and $n=2$ rendered very probable.

These chemical methods, though mostly sufficient in practice, are exposed to the logical objection that they depend on products of reaction, and that during the reaction a total transformation of the molecular complex might occur; e.g. the formation of acetic acid might be



and on the other hand can at most only give a probable minimum size for the molecule; it is therefore fortunate that the physical methods are suitable for directly testing the molecular weight of the bodies in question.

In the following collection of *physical methods for determination of molecular weight*, a selection has been made in accordance with the plan of the work. On the one hand are the methods based on Avogadro's law, and applicable to gases and solutions; on the other are methods applicable to liquids, of which that of Eötvös, Ramsay, and Shields, based on the change of surface tension with temperature, is an example; on account of the empirical character of the latter they will be found in Part III, which is concerned with the relations between properties (e.g. capillary constant) and composition (and therefore molecular weight). We shall therefore confine ourselves here to:—

- § 1. Molecular weight determination in dilute gases.
- 2. " " " " " " " solutions.
- 3. " " " " " " " solid solutions.

§ 1. MOLECULAR WEIGHT DETERMINATION IN DILUTE GASES.

A. Avogadro's Law.

It is well known that the law on which the determination of molecular weights in gases is based, as stated by Avogadro, is to the effect that equal volumes of dilute gases, measured

under the same temperature and pressure, contain equal numbers of molecules, and therefore the molecular weights of the gases are in proportion to the weights of those volumes.

The law in question, which, when first stated, was a happy combination of known facts, received confirmation in that it allowed of predicting new ones, such as the dissociation of ammonium chloride on volatilization. But it may also be deduced from the kinetic theory. As we shall bring forward the confirmations of the law later, under the head of 'results,' we will here begin with its theoretical deduction.

The kinetic theory of gases, treating gases as consisting of small, perfectly elastic spheres, involves Avogadro's law as the limiting case of extreme dilution. When the dilution is sufficiently great, the attractions between the molecules cease to be of account, and the volume of the molecules may be neglected in comparison with the total volume occupied by the gas. The deduction of Avogadro's law from the kinetic theory in the general case is complicated, and for the purpose of this work it is sufficient to follow it out under special simplifying circumstances.

In the first place, for simplicity it may be assumed that the velocity of all the molecules is the same, viz. C metres per second. Secondly, that the movement inside the cubical vessel of V cub. metres capacity (Fig. 1) that we shall consider, is so distributed that the molecules move only at right angles to the bounding planes, and equally so, there being always one-sixth of the N molecules moving forwards, backwards, right, left, up, or down. Hence there strike unit surface (one sq. metre) in unit time (one second), one-

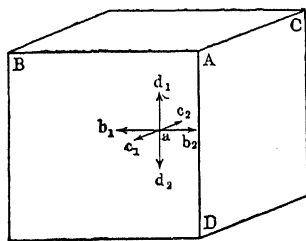


Fig. 1.

sixth of the molecules contained in a parallelopiped at right angles to the surface, and C metres long; i.e.

$$\frac{NC}{6V}.$$

They are repelled with equal velocity; so that the whole have in the second suffered a change of velocity of $2C$ metres per second. The force needed for that (P kilograms pressure per sq. metre) may, according to the law

$$\text{force} = \text{mass} \times \text{acceleration},$$

be calculated as

$$P = \frac{NC}{6V} M \times 2C = \frac{NMC^2}{3V} \text{ or } PV = \frac{1}{3} NMC^2,$$

where M is the mass of a molecule.

For two gases at the same temperature and pressure we have consequently:

$$(1) \quad N_1 M_1 C_1^2 = N_2 M_2 C_2^2.$$

The third condition, equality of temperature, includes, however, a further relation, for it may be shown that equality of temperature corresponds to equality of mean kinetic energy of the molecules, or

$$(2) \quad \frac{1}{2} M_1 C_1^2 = \frac{1}{2} M_2 C_2^2,$$

from which by combination with (1) we get

$$N_1 = N_2,$$

that is an equal number of molecules for equal volume, pressure, and temperature.

Before we describe the methods in which Avogadro's law may be applied, we may conveniently put it in a single mathematical form which expresses also the laws of Boyle and Gay-Lussac. It is well known that the last two may be represented by

$$PV = RT.$$

If the molecular quantity of different gases be taken, then according to Avogadro's law, as just stated, for equal pressure (P) and temperature (T), the volumes (V) will

also be equal, which amounts to saying that R referred to the molecular quantity has the same value for all gases.

Taking 2 kilograms of hydrogen as basis for calculating this value of R , we have for atmospheric pressure and 0°C .

$$P = 10333 \text{ kg/sq. m.} \quad T = 273 \quad V = \frac{2}{0.08956} \text{ cub. m.}$$

since one litre of hydrogen at 0° and atmospheric pressure weighs 0.08956 gm. Therefore

$$R = 845.2.$$

Since this number happens to be approximately twice the value of the calorie in kilogrammetres ($\frac{1}{A} = 423$) the expression for the laws of Boyle, Gay-Lussac, and Avogadro simplifies, approximately, to

$$APV = 2T.$$

B. Methods for Molecular Weight Determination in Gases.

1. Ordinary Process.

The application of Avogadro's law, formerly the only means of determining molecular weights, has, since the introduction of the simple methods based on the theory of solutions, been practically confined to Victor Meyer's process¹.

As in all such methods, the procedure consists essentially in measuring the volume (V) of a known weight (G) as gas or vapour under a definite pressure (P) and temperature (T). An equal volume of hydrogen would, under these circumstances, weigh

$$0.08956 PV \times \frac{273}{T} = 24.45 \frac{PV}{T}$$

if weight, volume, pressure, and temperature are given in

¹ *Berl. Ber.* 30. 1926.

grams, litres, atmospheres, and in absolute centigrade measure respectively. Since under the specified circumstances there is, according to Avogadro, proportionality between total weight and molecular weight, we get:

$$G : 24.45 \frac{PV}{T} = M : 2,$$

where M is the desired molecular weight, and 2 that of hydrogen (see p. 24).

In Victor Meyer's method a cylindrical vessel b (Fig. 2) of about 200 c.c. capacity, ending in a long neck with a side tube af , is filled with air or nitrogen, and brought to a convenient constant temperature. If now the weighed quantity of substance be introduced into the cylinder by means of the dropping arrangement d , the vapour produced expels an equal volume of air which passes through the side tube af and is collected in the graduated tube g over water.

The great advantage of this process is that it allows of the evaporation being performed at a very high temperature, which need not be exactly determined. Ignorance of this temperature has no influence on the result, as it is the temperature of the graduated tube, not that of the cylinder, that is needed to calculate the molecular weight.

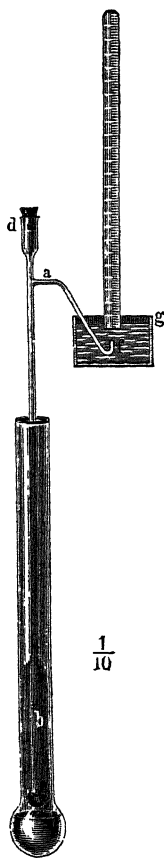


Fig. 2.

2. Determination of Vapour Density by means of the Second Law of Thermo-dynamics.

We will mention here a second method which, though, so far, of no consequence in the practical measurement of molecular weights of gases and vapours, may be of

interest at the present time in its special application to solutions.

The method is based on the application of the second law, which, as applied to the process of evaporation, was given (Part I, p. 19) as

$$AVdP = q \frac{dT}{T},$$

where A is the thermal equivalent of work = $4\frac{1}{3}$, V the increase in volume on evaporation, in cub. metres, of a quantity (say 1 kilogram) that absorbs q calories, P the pressure of the saturated vapour in kilograms per sq. metre. A vapour density—and therefore a molecular weight determination—may be obtained from this equation, since the volume of the vapour itself may be taken as V when the dilution of the saturated vapour is sufficiently great, so that the measurement of volume is based upon that of the change of vapour pressure with temperature, and the latent heat of evaporation. Taking water as an example, with the data:

$$P_{10} = 9.14 \text{ mm.}, \quad P_{20} = 17.363, \quad q_{15} = 584 \text{ cal.},$$

we get, without integration, using the formula

$$V = \frac{q\Delta T}{AT\Delta P} = \frac{584 \times 10}{288 \times 8.223 \times 13.6 \times A} = 77,$$

where 13.6 is the density of mercury. Now 77 cub. metres of hydrogen at 13.2515 mm. and 15° weigh

$$77 \times 0.08956 \times \frac{13.2515}{760} \times \frac{273}{288} = 0.114 \text{ kg.}$$

So that the molecular weight of water vapour according to Avogadro is

$$M : 2 = 1 : 0.114.$$

$$M = 17.6,$$

which is close to the known value $H_2O = 18$.

In the same way the observations for acetic acid show an abnormal molecular weight. We may perform the calculation in a simpler way by using, instead of the

kilogram as before, the molecular weight M as obtained from the vapour density. Then

$$AVP = 2T, \text{ so that } \frac{dP}{P} = \frac{Mq dT}{2T^2} \text{ or } M = \frac{2T^2 dP}{qP dT}.$$

Introducing the values

$$P_{10} = 6.6 \text{ mm.}, \quad P_{20} = 11.6 \text{ mm.}, \quad q = 85 \text{ cal.},$$

we have

$$M = \frac{2 \times 288^2 \times 5}{85 \times 9.1 \times 10} = 107$$

instead of 60 ($= \text{C}_2\text{H}_4\text{O}_2$), in accordance with the conclusion from direct vapour density measurements, that saturated vapour of acetic acid has a nearly double molecular weight, and consists mainly of double molecules.

C. Results.

1. *Connexion with the Atomistic Hypothesis.*

The fundamental scientific interest of the results obtained by application of Avogadro's law lies in the complete connexion that can be established between the chemically determined atomic weights and the molecular weights arrived at physically.

The necessary conclusion from atomistic reasoning, that in reactions the molecules concerned must be in whole number relationship, as e.g. when methane (CH_4) is burnt in nitrous oxide (N_2O)



agrees with Gay-Lussac's law that in reactions the volumes of gases concerned are in such a relationship. According to Avogadro the ratios in question may be read off the equation directly, in the form of the coefficients occurring in it, as each molecular symbol corresponds to the same volume, so that

$$\begin{aligned} \text{Vol. CH}_4 : \text{Vol. N}_2\text{O} : \text{Vol. CO}_2 : \text{Vol. H}_2\text{O} : \text{Vol. N} \\ = 1 : 4 : 1 : 2 : 4. \end{aligned}$$

This relation occurs most simply in the case of the elements. The ratio of their molecular weights, i. e. of their gas densities, must either be the same as that of their atomic weights, or, if the molecules are built up out of different numbers of atoms, be in integral relation to those. Exact proof of this is rendered difficult by the fact that Avogadro's law is only exactly true for infinite dilution. A recent extrapolation¹ in that direction leads to the conclusion that the densities of hydrogen, nitrogen, and oxygen on infinite dilution are in the ratio

$$1.0074 : 14.007 : 16,$$

whilst Ostwald gives for the atomic weights:

$$1.0032 : 14.041 : 16.$$

2. Confirmation and Testing of Atomic Weights.

The determination of atomic weights by purely chemical means is attended with an uncertainty, which may be noticed in the history of the atomic weights, and may be illustrated in the following way. Choosing as unity $H = 1$, or rather $O = 16$ as better suited for analytical purposes, the analysis of e. g. beryllium oxide with 36.3 per cent. beryllium is not conclusive as to the atomic weight of beryllium, but leaves it dependent on the formula of the oxide. If it is regarded as BeO we get

$$Be : O = 36.3 : 63.7 = x : 16;$$

$$x = 9.1;$$

whilst if Be_2O_3 is chosen—and both formulae have had their supporters—it follows that

$$2 Be : 3 O = 36.3 : 63.7 = 2x : 3 \times 16;$$

$$x = \frac{3}{2} \times 9.1.$$

The decision here and in corresponding cases has in the end rested on determinations of molecular weight. The determination is not possible for the oxide on account of its

¹ D. Berthelot, *Compt. Rend.* 126. 954.

non-volatility, but can be made with the chloride. The molecular weight of the latter, according to the respective assumptions, would be

$$M_{\text{BeCl}_2} = 9.1 + 71 = 80.1, \quad M_{\text{BeCl}_2} = \frac{3}{2} \times 9.1 + 106.5 = 120.$$

The former number was found by Nilson and Petterson¹ and the atomic weight 9.1 so finally settled. The only change possible would be a halving, &c., of this atomic weight, so that the method gives a maximum value, below which there is neither chemical nor physical reason for going, and which has, moreover, received confirmation in another way (p. 26).

3. *Nature of the Elementary Molecules, and Polymerism.*

Polyatomicity. Hydrogen. One of the leading results of molecular study of the elements is the fact that their molecules usually consist of more than one atom. Thus, the two facts that prove this for hydrogen are:

The density of hydrochloric acid is 18.25 referred to hydrogen, and it contains 2.74 per cent. of hydrogen.

Since the densities, according to Avogadro's law, are in the ratio of the molecular weights, we conclude from these data that the ratio between the amounts of hydrogen present in the hydrogen and hydrochloric acid molecules is

$$1 : 18.25 \times \frac{2.74}{100} = 2 : 1.$$

Thus there is twice as much hydrogen in a hydrogen molecule as in one of hydrochloric acid, and as the latter cannot contain less than one atom of hydrogen, there must be at least two in the hydrogen molecule. Such reasoning has in no case, so far, led to the necessity of assuming more than two atoms in the hydrogen molecule, so it may be regarded as diatomic, with the symbol H_2 . For that reason hydrogen, with $M=2$, is usually chosen as unit for molecular weight determinations.

¹ See also Rosenheim and Woge, *Zeitschr. f. anorg. Chem.*, 15, 283.

Most of the elements studied are, like hydrogen, diatomic; only a few have more atoms, as phosphorus P_4 , arsenic As_4 , sulphur S_8 .

Monatomic elements. Mercury. Especially interesting are the cases in which the elementary molecule is, according to the above reasoning, to be regarded as monatomic. This was first shown to be probable for mercury; since then other metals (zinc, cadmium, potassium, sodium) have been studied in the state of vapour, and appear to behave similarly; and the newly discovered elements, argon and helium, belong to the same category. Mercury, moreover, was the subject of an important experiment by Kundt and Warburg, which, by the aid of a deduction from the kinetic theory, confirms the conclusion of monatomicity. The experiment refers to the ratio between the specific heats at constant pressure and constant volume. The latter has obviously the smaller value, and in the case of monatomic gases represents the increase in kinetic energy of the molecular movement; in polyatomic gases it includes also an increase in the atomic movements, more difficult to calculate. According to the previous equation

$$PV = \frac{1}{3} NMC^2$$

the kinetic energy

$$\frac{1}{2} NMC^2 = \frac{3}{2} PV,$$

so that its increase per degree is

$$\frac{3}{2} aPV,$$

where $a = \frac{1}{273}$.

If free expansion (at constant pressure) takes place, we are concerned with the specific heat at constant pressure, and additional heat is required to perform external work, which obviously amounts, per degree, to

$$aPV.$$

The ratio of the two specific heats is therefore

$$\frac{3}{2} aPV + aPV : \frac{3}{2} aPV = 5 : 3 = 1.67,$$

whilst for polyatomic gases it is less, since the term $\frac{3}{2}aPV$ will be greater on account of the kinetic energy of the atomic movements. It is well known that measurements of the velocity of sound gave the expected value 1.67 for mercury vapour, and lower values for polyatomic gases.

As according to p. 24 the atomic weights so far found are strictly to be regarded as maxima, we have now an indication from thermal reasoning that, at least for mercury, the maximum has not been placed too high.

Allotropy of the elements. Ozone and oxygen. A third important result of molecular weight measurements of the elements has been to show, on grounds of the molecular-atomistic hypothesis, the existence of the same element in different, so-called allotropic, forms. Oxygen and ozone form the most striking example. Soret proved that ozone, on conversion into oxygen, increased in volume by one-half, so that oxygen being diatomic, ozone is to be regarded as O_3 , the equation



indicating the increase in the number of molecules by one-half, and according to Avogadro, increase of volume in the same ratio.

Dissociation of the elements at high temperature. The halogens. A very welcome confirmation of the above views on the polyatomicity of the elements is given in the proof of the possibility of decomposing those molecules. Even sulphur, which at low temperatures appears as S_8 , shows an abnormal expansion up to $1,000^\circ$, leading by then to a density corresponding to S_2 . A further step in this direction was accomplished by Victor Meyer for the halogens, since he showed that iodine, which under 600° has a density corresponding to the diatomic molecule I_2 , becomes halved in density above $1,400^\circ$, with formation of monatomic molecules or free atoms.

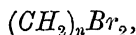
It may be added that in this direction lies the possibility, if any, of decomposing the elements themselves: the monatomic molecule constitutes the last stage towards the

undecomposed fundamental material; if the structure can be still further simplified, then a further decomposition is attainable. This is exactly the point of view adopted by Victor Meyer in his latest researches. In his Lübeck address on 'Problems of Atomistics' (1896) he referred to this aim. After that, and until the end of his life, he occupied himself with experiments in this direction¹, and had in view molecular weight determinations up to 2,000°. The glass vessels had long been replaced by others of porcelain, and this material by platinum or the still more infusible alloy with 25 per cent. iridium. Finally vessels of magnesia were prepared, which, in a lime oven, stood the temperature of 2,000° obtained by burning graphite in oxygen. But no further decomposition than that into monatomic elements was reached in the case of any element.

Polymerism. The difference in molecular weight associated in the elements with differences of properties occurs also, it is well known, in compounds of the same compositions, especially in organic chemistry, and is then called polymerism. Whole series of similarly composed bodies, such as



are known, in which n varies from 2 to 30, accompanied by a corresponding change in vapour density and chemical behaviour, as e. g. in combination with bromines, the bodies



of different composition, arise.

§ 2. MOLECULAR WEIGHT DETERMINATION IN DILUTE SOLUTIONS.

Since the possibility of molecular weight determinations of gases and vapours was shown by Avogadro, the modern development of the theory of solutions rendered the same

¹ *Berl. Ber.* 30. 1926.

thing possible for these latter substances. We will therefore next develop that theory, and then, in connexion with it, give the methods for determination of molecular weight, with their results and applications.

A. The Theory of Dilute Solutions.

Whilst for the determination of molecular weight in dilute gas Avogadro's law can be applied directly, for dilute solutions the most varied methods, based on measurements of freezing points, boiling points, and vapour pressures, are in use. All these methods, however, may be brought into connexion with, and regarded as deductions from a law exactly corresponding to that of Avogadro, but which refers to osmotic instead of gas pressure; the law states, in fact, that solutions that exert the same osmotic pressure at the same temperature contain equal numbers of dissolved molecules in unit volume. This law may be arrived at in various ways. We shall here start from the molecular properties of known gases, and follow the deduction through gaseous solutions.

1. *Henry's Law and the Constitution of the Dissolved Gas.*

Take any gas of known molecular constitution, e.g. nitrogen (N_2) and a liquid, water, in which it is capable of solution, and consider the question whether the dissolved nitrogen corresponds to the formula N_2 or possibly is present as N or N_4 or as a hydrate. We have then to consider the equilibrium that is set up when the water B (Fig. 3) is saturated with the nitrogen A under the existing conditions of temperature and pressure. Kinetically considered, this equilibrium is based on the fact that, in unit time, as many gaseous molecules enter the solution B as leave the latter ¹.

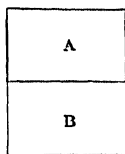


Fig. 3.

¹ In the following considerations the vapour of the solvent, present in A, may be supposed absent, by covering B with a membrane permeable

But from this a conclusion may be drawn if the nitrogen present in B consist entirely of molecules N_2 , i. e. is of the same constitution as in the gas. For if the quantity per unit volume in A is doubled, that in B must be so too, for, with sufficient dilution, this change would double both the number of gaseous molecules passing from A into B and the number of dissolved molecules passing from B into A. So that in this case the concentration C in the solution is proportional to the pressure P of the gas

$$C = kP$$

—a law that, under the name of Henry's law, is known to be applicable to the majority of gaseous solutions.

Let us now suppose a different case: first, that nitrogen is present in water as N, not as N_2 ; then the law of absorption becomes different also. In order to deduce this modified law, let us assume that in the gas too a certain quantity, even though vanishingly small, of nitrogen occurs as N; then between that and the nitrogen in the water there must be an equilibrium as in the preceding case, and proportionality as before—

$$C = k_1 P_N,$$

where P_N is the very small partial pressure of the gaseous nitrogen in the form N. This partial pressure is not, however, proportional to the total pressure P , since the equilibrium in the gas between the two forms of nitrogen, according to the equation



is subject, according to the laws of chemical equilibrium (cf. Part I, p. 109), to the relation

$$P_{N_2} = KP_N^2,$$

where P_{N_2} and P_N are the partial pressures of the nitrogen in the forms N_2 and N respectively, and consequently P_{N_2}

to nitrogen, but not to water vapour; although if the vapour were present the reasoning would still hold.

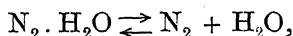
differs only by a vanishingly small amount from the total pressure P . Hence

$$P = KP_N^2 \text{ and } C = k_1 P_N = k\sqrt{P},$$

where k is a constant, equal to k_1/\sqrt{K} .

In this case, then, the concentration of the dissolved substance would not be proportional to the pressure of the gas, but to its square root, which would imply a very wide departure from Henry's law: quadruple pressure would not involve a quadrupling of the concentration, but only a doubling.

A different molecular constitution, such as N_3 or N_4 , would introduce a corresponding change in the law, so that there only remains to consider the case of hydrate formation, such as $N_2 \cdot H_2O$. This case may be treated in a similar manner, by assuming the presence in the gas of an extremely small quantity of the hydrate, or in the solution of, besides hydrate, an extremely small quantity of nitrogen not combined with water. Both assumptions lead to the same result; by assuming a small amount of hydrate in the gas, we bring into play the equilibrium



with the condition

$$P_{N_2 \cdot H_2O} = KP_{N_2},$$

in which $P_{N_2 \cdot H_2O}$ and P_{N_2} are the partial pressures of the hydrate and of free nitrogen respectively. Since obviously

$$P_{N_2} = P - P_{N_2 \cdot H_2O}$$

the equation may be replaced by

$$P_{N_2 \cdot H_2O} = K_1 P,$$

where

$$K_1 = \frac{K}{1 + K}.$$

Since according to what preceded, the partial pressure of the hydrate is proportional to the concentration of the

dissolved nitrogen, we get a ratio between pressure and concentration

$$C = kP,$$

exactly as if the nitrogen were dissolved in the form N_2 instead of $N_2 \cdot H_2O$. Hence the presence of a hydrate has no influence on the law of absorption; and generally that of any hydrate $N_a(H_2O)_b$ does not differ from solution of the water-free molecule N_a .

We may therefore conclude that gases which on solution follow Henry's law, possess the same molecular weight in the solution as in the gaseous state, with only the possible exception that hydrate formation, always without change in size of the gaseous molecule, may occur. As already remarked, nearly all the gases whose absorption has been studied belong to this category: N_2 , H_2 , O_2 , CO_2 , CO , N_2O , CH_4 , C_2H_4 , H_2S , NO , C_4H_{10} , C_2H_6 in water and alcohol; CO_2 in carbon disulphide and chloroform; C_2H_2 in acetone¹. Indications of a different behaviour occur with NH_3 and SO_2 in water, while HCl in water departs so far from Henry's law that an entirely altered molecular magnitude on solution is to be concluded.

2. Avogadro's Law for Dissolved Substances.

What for our purpose is essential in the preceding argument is not that the molecular weight of some ten or twelve gases in solution is known, but the principle that if Henry's law of absorption answers to the facts, then a gas does not change its molecular magnitude on going into solution. On account of the limited data available on absorption, and especially on account of the fact that most substances are too involatile to give gases or vapours of measurable density, the principle discussed is of minor importance in its direct application. We have rather to consider the question—without assuming any experimental data on absorption—what property must any dissolved

¹ *Compt. Rend.* 124. 988.

body possess as gas or vapour, in order that it may, on absorption, follow Henry's law? and the answer is that the gas or vapour must, at equal temperature and concentration, exercise a pressure equal to the osmotic pressure of the same substance in the dissolved state.

The proof of this may be given in a form due partly to me¹, partly to Lord Rayleigh², and partly given in a private correspondence with Dr. Donnan.

Before entering on the proof, which deals with osmotic pressure and semipermeable membranes, i.e. membranes that only allow the solvent to pass, it may be remarked that any notion one may form as to the mechanism producing osmotic pressure, or the action of semipermeable membranes, is without influence on the reasoning. Thus the question whether the pressure is produced by the

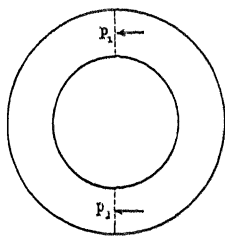


Fig. 4.

solvent or by the dissolved body can be left out of consideration; so too, whether it is dependent on collisions or by attractive forces. The action of the membrane too, whether it is as a sieve, or by means of absorption, is indifferent. All this is the case because the proof to be given is based on thermo-dynamics, and is consequently free from assumptions on the mechanism. Moreover it is plain that two semipermeable membranes cannot give different osmotic pressures, for that would allow of a *perpetuum mobile*; thus let the ring (Fig. 4) be supposed filled with solution on the right, and solvent on the left, separated by two semipermeable membranes above and below, which give osmotic pressures amounting to p_1 and p_2 respectively. Such a difference of pressure $p_1 - p_2$ would then give rise to a flow, which, as all the conditions remain unchanged, would never cease.

After these remarks, let us proceed to the actual proof. By means of a reversible cyclic process carried out at

¹ *Zeitschr. f. Phys. Chem.* 1. 488.

² *Nature*, 55. 253.

a constant temperature T , a kilogram of dissolved substance X is to be removed from, say, an aqueous solution in the form of gas or vapour, and restored to it again.

The removal of the dissolved body X is to take place by means of semipermeable membranes: the solution is separated from the undissolved gaseous X by the partition bc (Fig. 5), which only allows the gas to pass, whilst the pure solvent may be supplied through the walls ab and cd , on the outside of which is solvent.

Gas or vapour pressure and osmotic pressure are to be kept in equilibrium by means of two pistons, above and below. Now 1 kilogram of the dissolved body X occupies under temperature T and pressure P (kg. / sq. m.) a volume of V cub. metres. The ratio of absorption is such that this vapour is in equilibrium with a solution

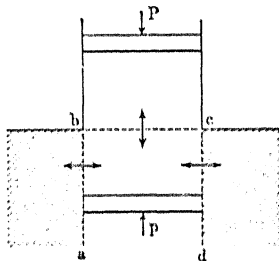


Fig. 5.

that contains 1 kilogram of X in v cub. metres, which solution exercises an osmotic pressure p (kg. / sq. m.). If now both pistons be moved upwards, 1 kilogram of X may be removed reversibly from the solution, an amount of work being done by it

$$PV = RT \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

whilst an amount of work is performed against the osmotic pressure, which we will express with the negative sign as

$$-pv \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

A second process now, will restore the vapour of X to the solution. First let the vapour expand to a very great volume V_∞ and in so doing perform work

$$\int_v^{V_\infty} PdV = RT \int_v^{V_\infty} \frac{dV}{V} = RT \log \frac{V_\infty}{v} \quad . \quad . \quad (3)$$

The so diluted vapour may now be brought into contact

with a volume v of water, a process which, in the limiting case in which V_∞ is infinite, is reversible, for under those circumstances the water would not absorb any of the infinitely dilute vapour X . Now let the piston be lowered and so X be brought into solution, with an expenditure of work

$$-\int_0^{V_\infty} P_1 dV_1.$$

Here, however, P_1 has not the value given by

$$P_1 V_1 = RT,$$

but a smaller value, because a part of the vapour has gone into solution. This part is exactly 1 kilogram when the pressure has risen to P , and consequently, if Henry's law of absorption is true, when the pressure is P , amounts to P_1/P kilograms; the undissolved part remaining is therefore $1 - P_1/P$, and the pressure P may be calculated from

$$P_1 V_1 = \left(1 - \frac{P_1}{P}\right) RT = RT - P_1 V,$$

so that

$$P_1 = \frac{RT}{V_1 + V}.$$

Consequently the work done is

$$-\int_0^{V_\infty} P_1 dV_1 = -RT \int_0^{V_\infty} \frac{dV_1}{V_1 + V} = -RT \log \frac{V + V_\infty}{V},$$

which, if V_∞ is infinitely great, becomes

$$-RT \log \frac{V_\infty}{V} \quad \dots \dots \dots (4)$$

Since the total work done in a reversible cyclic process at constant temperature must be zero

$$(1) + (2) + (3) + (4) = RT - pv + RT \log \frac{V_\infty}{V} - RT \log \frac{V_\infty}{V} = 0$$

or

$$pv = RT.$$

By comparison with

$$PV = RT,$$

since T is constant, we see that for equal values of V and v we must have

$$P = p.$$

This is the result originally referred to, that any dissolved body which obeys Henry's law, must have such properties that for equal temperature and concentration, the gas pressure and the osmotic pressure must be equal.

But we know, by what precedes, that a vapour dissolving according to Henry's law must have the same molecular character in the solution and the vapour, and consequently we may draw all the conclusions as to the osmotic pressure of dissolved bodies that have been drawn as to gas or vapour pressure, i. e. we may apply Avogadro's law to solutions, making use of the osmotic pressure instead of the gas pressure.

From this necessary equality of gas and osmotic pressure for similarity of molecular constitution in solution, it follows that the osmotic pressure obeys the gaseous laws, i. e. the laws of Boyle and Gay-Lussac. A remark on the nature of the osmotic pressure may be made here; if it follows Gay-Lussac's law, and is so proportional to the absolute temperature, it, like gas pressure, becomes zero at the absolute zero of temperature, and consequently vanishes when the molecular movements come to rest. It is, therefore, natural to look for the cause of osmotic pressure in kinetic grounds, and not in attractions.

A second general remark may be made in connexion with the gaseous laws as applied here. In this case too they are to be regarded as limiting approximations, only strictly true for infinite dilution. They refer, on account of the kinetic nature of the osmotic pressure, to that part of it which prevails on increase of dilution; whilst, when the concentration is greater, the attraction of the solvent becomes of more consequence, and eventually must prevail, since it increases in proportion to the square of the concentration, while the number of molecular collisions is only proportional to the first power.

B. Methods for Molecular Weight Determination of Dissolved Bodies¹.

As in gases a measurement of molecular weight involves a knowledge of the weight, volume, pressure, and temperature in the gaseous or vaporous condition, so in solutions the same four data suffice, the osmotic pressure replacing the ordinary pressure.

From the theoretical point of view, the first thing to consider is the osmotic pressure itself; but in practice indirect methods involving quantities related to that pressure occur; we shall therefore discuss in turn the direct and indirect methods of molecular weight determination for dissolved bodies.

1. *Direct Methods for Molecular Weight Determination of Dissolved Bodies.*

(a) *Comparison of the osmotic pressure of different solutions (Isotony).* Whilst for gases the determination of molecular weight is an easy operation, for solutions a direct application of the corresponding laws meets with the difficulty of measuring osmotic pressure—a difficulty due to the necessary use of a semipermeable membrane, i.e. a wall or boundary permeable to the solvent but not to the dissolved body. If the absolute value of the osmotic pressure is to be measured, the 'membrane' has, in addition, to stand a mechanical pressure which may be great, which makes the experiment still more difficult; we shall, therefore, first describe the methods in which this difficulty, due to pressure, is avoided by observing, instead of the actual osmotic pressure of a solution, equality between two solutions of equal osmotic pressure; afterwards the

¹ Verschaffelt, *Le poids moléculaire de l'eau et de l'ode*; Acad. des Sciences de Belgique. Bruxelles, 1896. Biltz, *Praxis der Molekulargewichtsbestimmung*, Berlin, 1898.

few direct measurements that have been carried out will be mentioned.

First, as to the semipermeable membrane. The peculiar property of allowing one substance to pass, and not the other, seems to depend not so much on sieve-like action as on the ability to dissolve or absorb, or loosely combine with one substance. Such a selective action occurs with gases, e.g. palladium¹ allows the passage of hydrogen, which is absorbed by it. Nernst² has described a semipermeable membrane for liquids, based upon the same principle, and consisting of an animal membrane, moistened with water, placed between (moist) ether on one side, and (moist) ether, in which benzene was dissolved, on the other. The ether, being slightly soluble in water, passes through the membrane towards the side containing benzene, whilst the benzene, insoluble in water, fails to pass through. Quite recently the property of caoutchouc, noticed by Graham, of transmitting certain gases, such as sulphur dioxide and carbon dioxide, has been studied with regard to liquids³: whilst e.g. methyl and ethyl alcohol cannot permeate the caoutchouc, ether, carbon disulphide, chloroform, benzene, &c., can, so that if one of these liquids be placed on one side of the membrane, and methyl alcohol on the other, ether, &c., passes through. Moreover, it has been shown that the rate at which the transmission takes place is in agreement with the rate at which the liquid in question is absorbed by caoutchouc. Finally, Tammann discovered in the zeoliths a material permeable only for water—not for substances dissolved in it; these zeoliths are known to be hydrated silicates, which, according to Mallard, possess the peculiar property of absorbing and giving up water, without losing their crystalline form.

Whilst those membranes are of importance for the explanation of semipermeability, an entirely different material

¹ Ramsay, *Zeitschr. f. Phys. Chem.* 15. 518; Hoitsema, l. c. 17. 1.

² Nernst, l. c. 6. 38.

³ Raoult, *Comptes Rendus*, 121. 187; Fusin, l. c. 121. 794.

has been used for actual measurements, viz. so far, membranes occurring in animal and vegetable tissue, the precipitate discovered by Traube.

The membranes in animal and vegetable organisms offer little resistance, have proved especially useful as semipermeable partitions, and an example of each is given here. In the first place we have the protoplasmic sheath of the plant cell¹, an elastic membrane freely against the cell-wall, being kept against it by the osmotic pressure of the contents. If, however, the cell is placed in a salt solution of high osmotic pressure, the cell contracts away from the cell-wall: the process known as plasmolysis occurs, as may be very well seen with *Tradescantia* cells. Different solutions that exercise so high an osmotic pressure as just to produce plasmolysis, are equal in their osmotic action, are so-called isotonic, and therefore, according to Avogadro's law as extended to solutions, contain equal numbers of dissolved molecules in the same volume. e. g. a solution containing 5.96 per cent. of raffinose was found isotonic with a solution of cane-sugar ($C_{12}H_{22}O_{11}$, 342) containing 0.1 gm. mol. per litre (i. e. 3.42 %). The molecular weight of raffinose must be approximately

$$3.42 : 5.96 = 342 : x \quad x = 596,$$

and as for raffinose the choice lay between $C_{18}H_{32}O_{16} \cdot 3H_2O = 396$ (Berthelot and Ritthausen), $C_{18}H_{32}O_{16} = 594$ (Loiseau and Scheibler), and $C_{36}H_{64}O_{32} \cdot 10H_2O$ (Tollens and Rischbiet), this was decisive in favour of the second formula, a conclusion which has since been confirmed by chemical means, since raffinose takes up water and decomposes into three molecules of sugars, each containing six carbon atoms (glucose, laevulose, and galactose) :



¹ De Vries, *Zeitschr. f. Phys. Chem.* 2. 440.

A similar determination of isotony by physiological means, in this case, however, taken from the animal organism, may, according to Hamburger¹, be carried out with red blood corpuscles, the solution to be studied being shaken up in a test tube with a couple of drops of defibrinized blood. Two phenomena are then observed, according as the solution exercises a great or small osmotic pressure: in the first case the corpuscles give up their colouring matter to the solution; in the second they sink to the bottom of the colourless liquid. Liquids which lie on the margin in this respect are isotonic, and so we have an easily available means for molecular weight determinations.

Similar isotony has been observed by Tammann² without physiological aid, by means of a precipitated membrane, that is a colloidal skin formed by contact of two solutions. The most available material yet found for this purpose is copper ferrocyanide, obtained by contact of potassium ferrocyanide and copper sulphate in layers; this was used, and the passage of water in one or the other direction observed by means of Töpler's interference apparatus: where water enters, a rising stream in the specifically heavier salt solution is observed; where the reverse occurs, a descending stream due to local increase in density.

(b) *Absolute Measurement of Osmotic Pressure.* As already mentioned, absolute pressure measurements of osmotic phenomena are rendered difficult by the fact that it is not only necessary to prepare a semipermeable partition, but one that has sufficient resistance to stand the commonly great mechanical pressures involved. The organic membranes, which were found so well adapted for determining isotony, are for that reason useless for the present purpose, and consequently there are only a few isolated experiments that have been carried out with success,

¹ *Zeitschr. f. Phys. Chem.* 6. 319.

² *Wied. Ann.* 34. 299.

but which, however, are of the highest importance in testing the laws of osmotic action.

We may first mention a measurement of Ramsay on gases¹ which is very instructive as to the mechanism by means of which osmotic pressure is produced. A palladium

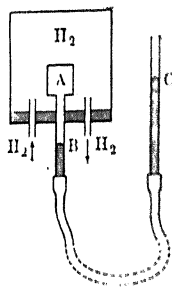


Fig. 6.

vessel A (Fig. 6) constituted the membrane and contained nitrogen, whose pressure could be measured, as shown in the figure. A was then surrounded by a stream of hydrogen at known pressure, and the pressure inside A rose, on account of the gas passing through the palladium partition, by an amount nearly equal to the external hydrogen pressure (would perhaps have coincided with it if the external atmosphere had not originally

contained more hydrogen). Therefore the (osmotic) excess of pressure of the (dissolved) nitrogen present in the hydrogen corresponded to the pressure of the nitrogen alone (as Avogadro's law applied to solutions required).

Next we have Pfeffer's measurements of solutions. He used a semipermeable membrane of copper ferrocyanide, but gave it sufficient strength by depositing it inside a small porous battery-cell, the cell (moistened) being filled with potassium ferrocyanide, and dipped in copper sulphate. Diffusion from both sides then brings about the formation of the membrane. With such an apparatus the following measurements were carried out on a one per cent. sugar solution (1 gm. in 100.6 c.c.).

Temp. (t)	osm. press. P	$M = 0.0114 \cdot \frac{273(t+273)^2}{P}$
7°	0.664 atm.	344
14	0.681 "	344
22	0.721 "	344
32	0.746 "	346
36	0.746 "	347

¹ *Zeitsch. f. Phys. Chem.* 4, 548

² *Osmotische Untersuchungen*. Leipzig, 1897.

From these data the molecular weight M may be calculated on the basis of Avogadro's law according to the relation (p. 19)

$$G : 24.45 \frac{PV}{T} = M : 2,$$

where G is the weight in grams ($= 1$), V the volume in litres (0.1006), so that

$$M = 0.813 \times \frac{273+t}{P}.$$

The numbers thus calculated are given in the last column, and are in good accord with the number, 342, obtained from the formula of sugar, $C_{12}H_{22}O_{11}$. Notwithstanding this and several other researches¹, direct measurement of osmotic pressure has not yet led to a practicable method for determining molecular weights.

2. Indirect Methods for Molecular Weight Determination.

Whilst direct measurement of the osmotic pressure has so far met with difficulties for want of a satisfactorily resistant semipermeable membrane, so that the experiment is difficult or even impossible, attention has been paid to other properties of solutions, which bear calculable relations to the osmotic pressure.

With regard to these methods, we may say generally, with Nernst, that every mode of separation between solvent and dissolved body involves a method for determination of molecular weight. This is so because every such separation renders possible a cyclic process in which the solvent, after having been separated in the way in question, may be again brought together with the separated or dissolved substance osmotically, i. e. by means of a semipermeable membrane. If this cyclic process be carried out reversibly—e. g. if the osmotic action be supposed to take place in a cylinder with piston, such that the wall of the cylinder enclosing the

¹ Ladenburg, *Berl. Ber.* 22. 1225; Adie, *J. C. S.* 1891, p. 344; Ponsot, *Compt. Rend.* 125. 867; Naccari, *Rend. Acc. Lincei*, 1897, 1. 32.

solution is semipermeable, and the piston exercises a pressure exactly equal to the osmotic pressure then a thermo-dynamic relation may be deduced which involves the possibility of measuring the molecular weight.

Viewed from this point of view, the indirect methods for determination of molecular weights may be divided into two groups, according as the cyclic process underlying them can be carried out at constant temperature or not; in the first case the theoretical argument is simpler, and can often be simply demonstrated without the aid of thermodynamics.

(a) *The cyclic process can be carried out at constant temperature. Molecular weight determination by vapour pressure measurement.* The common character of methods based on cyclic processes which can be carried out at constant temperature is that they can be performed at any temperature, whether the separation be as vapour or by shaking with a third substance. We have, however, to distinguish as distinct methods the separation of solvent and of dissolved substance, and so we arrive at the following *résumé*:—

1. Separation as vapour.

(a) The dissolved substance separates out: phenomena of absorption.

(β) The solvent separates out: lowering of vapour pressure.

2. Separation by a solvent.

(a) The dissolved substance separates out: ratio of partition.

(β) The solvent separates out: lowering of solubility.

With regard to the first of these methods, based upon the phenomena of absorption, we may refer to p. 28, and only note that when Henry's law of absorption holds (proportionality between pressure of the gas and concentration in solution) the absorbed gas in question must exist with unchanged molecular weight in solution.

We must now deal with the second method, based on the

lowering of vapour pressure produced by the dissolved body.

The vapour pressure of a solution is immediately related to its osmotic pressure. Obviously two solutions in the same solvent, if they have the same osmotic pressure, i. e. are isotonic, must show the same saturation pressure. Otherwise a *perpetuum mobile* in the meaning of Fig. 7 would be inevitable. The two isotonic solutions A and B are supposed separated by a semipermeable membrane; then if there is a difference between their saturation vapour pressures, a current of vapour will flow in the upper part of the vessel, say from left to right. Then the decrease and increase of concentration produced in B and A respectively will cause a movement of the solvent through ab from right to left, and so the conditions for a perpetual motion are given, which can only be avoided if isotony goes with equality of vapour pressure.

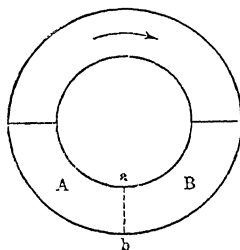


Fig. 7.

But further, the magnitude of the change in vapour pressure which a solvent suffers in taking up a dissolved body may be calculated, as will be clear from what follows.

Deduction of the law of diminution of vapour pressure without thermo-dynamics. We will first give the simple proof, due to Arrhenius, which does not involve thermo-dynamics. Suppose osmotic equilibrium to be established by means of the semipermeable membrane ab (Fig. 8), above which the solution rises to the height AB . Now the equilibrium implies that the solvent should not pass by distillation into or out of the solution.

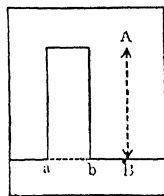


Fig. 8.

But the pressure, which at B equals the saturation pressure p of the solvent, is less at A by the pressure exerted by the

column of vapour AB ; accordingly, the saturation pressure of the solution which obtains at A must be less than that of the solvent, by—say— Δp . But just as the diminution of vapour pressure corresponds to the column of vapour, so the osmotic pressure corresponds to the column of liquid resting on ab , and if both be referred to the same area, the change of vapour pressure is to the osmotic pressure as the weight of any volume of vapour is to that of the same volume of liquid. Taking, for simplicity, a kilogram-molecule M of vapour, if its volume is v litres, then by applying Avogadro's law to the vapour and solution we get

$$pv = PV, \text{ so that } v = \frac{P}{p} V,$$

where p and P are respectively the vapour pressure and the osmotic pressure, and V is the volume in litres of a kilogram-molecule of the dissolved substance. If the composition of the solution is given as n molecules of dissolved substance to N molecules of solvent, one dissolved molecule m occurs in $m + \frac{N}{n}M$ kilograms of solution (here the molecular weight of the solvent is taken as M , as determined from the vapour density, but without any assumption as to the real value of that quantity in the liquid). If N is great, as in dilute solutions, the weight may be taken as $\frac{NM}{n}$; this is accordingly the weight of the volume V of solution, and that of v is $\frac{P}{p} \cdot \frac{NM}{n}$.

Hence we have the relation

$$P : \Delta p = \frac{PNM}{pn} : M$$

or

$$\frac{\Delta p}{p} = \frac{n}{N}.$$

This is a somewhat modified form of Raoult's law. The latter refers to the so-called molecular lowering of vapour

pressure, i.e. the value of $\Delta p/p$ obtained for a one per cent. solution multiplied by the molecular weight of the dissolved substance, or

$$\frac{\Delta p}{p} m = \frac{n}{N} m,$$

in which one part of dissolved substance is contained in 100 parts of solvent :

$$nm : NM = 1 : 100 \text{ or } \frac{nm}{N} = 1.01 M,$$

whence

$$\frac{\Delta p}{p} m = 0.01 M;$$

in other words, the relative lowering of the vapour pressure is equal to one hundredth of the molecular weight of the solvent; in which it must be borne in mind that the latter quantity has the value derived from vapour density measurements.

The following table shows results obtained for moderately dilute solutions¹ :

<i>Solvent</i>	<i>M</i>	$\frac{\Delta p}{p} m$
Water	18	0.185
Phosphorus trichloride	137.5	1.49
Carbon disulphide	76	0.8
Carbon tetrachloride	154	1.62
Chloroform	119.5	1.3
Amylene	70	0.74
Benzene	78	0.83
Methyl iodide	142	1.49
Methyl bromide	109	1.18
Ether	74	0.71
Acetone	58	0.59
Methyl alcohol	32	0.33
Mercury ²	200	2.

It may be remarked that, as with all rules derived from the theory of solutions, it is only strictly true for infinite dilution. For that reason we will now repeat the proof

¹ Raoult, *Compt. Rend.* 87. 167.

² Ramsay, *Zeitschr. f. Phys. Chem.* 3. 359.

with the aid of thermo-dynamics, insisting again that the law of the lowering of vapour pressure infers nothing as to the molecular weight of the liquid solvent.

Thermo-dynamic deduction of the law of diminution of vapour pressure. Let the solution contain da kilograms of dissolved substance in one kilogram of solvent, the former possessing the molecular weight m ; withdraw from it, osmotically and reversibly, i. e. with the aid of cylinder and piston, so much solvent as contains one kilogram-molecule of dissolved substance, with expenditure of work

$$AVdP = 2T,$$

where dP is the osmotic pressure in kilograms per square metre produced by the absorption into the solution of da per kilogram, and V the volume in cubic metres in which one kilogram-molecule is dissolved.

The amount of solvent withdrawn is to be restored reversibly by evaporation and condensation. In the first place we gain a quantity of work (1) by reversible evaporation at p and T ; next a second quantity by expansion of the vapour till the pressure has fallen to $p-dp$, that of the solution. This work, for the kilogram-molecule M of vapour, is

$$Avdp = 2T \frac{dp}{p};$$

consequently, for the mass $\frac{m}{da}$ with which we are concerned,

$$\frac{2Tdp}{p} \cdot \frac{m}{Mda}.$$

Finally the vapour is to be condensed in contact with the solution at $p-dp$ and T , in which process the work gained in (1) is used up. Since this cyclic process has been carried out at constant temperature, it cannot be accompanied by a conversion of work into heat, or vice versa, so that the

osmotic work spent must be equal to the work of expansion gained, i. e.

$$2T = \frac{2Tdp}{p} \cdot \frac{m}{Mda},$$

or

$$\frac{dp}{p} m = Mda,$$

which again comes to Raoult's law, if we remember that the solution contains da to one or $100da$ per cent. Accordingly, for a one per cent. solution, assuming the proportionality between concentration and lowering of vapour pressure which is true for infinite dilution to hold, we have

$$\frac{\Delta p}{p} m = \frac{dp}{p} \cdot \frac{m}{100da} = 0.01M.$$

In the same way as before we arrive at the expression

$$\frac{\Delta p}{p} = \frac{n}{N}.$$

The meaning of this equation may be illustrated by answering the question, 'What fall of vapour pressure does 1 % of sugar produce in water at 100° ?' Here $p = 760$ mm. and

$$n : N = \frac{1}{342} : \frac{100}{18} = \frac{1}{1900},$$

so that

$$\Delta p = \frac{760}{1900} = 0.4 \text{ mm.}$$

Abnormal values for abnormal vapour densities. There is another essential point to be noticed, viz. that N , the so-called number of molecules of solvent used in the deduction, is not always the real number; rather N is the fictive number of molecules obtained by taking the molecular weight of the saturated vapour at the temperature considered as unity. If the vapour, then, has an abnormal density, the abnormal molecular weight so obtained is to

be used in calculating N , as Raoult and Recoura¹ showed to be the case for acetic acid. They measured, as explained above, the relative molecular lowering of vapour pressure, i.e. the lowering for a one per cent. solution multiplied by the molecular weight of the dissolved substance, or in Raoult's nomenclature

$$\frac{f - f'}{f' P} m,$$

where P is the percentage content of solution, $f - f'$ the lowering of vapour pressure. This molecular diminution, multiplied by 100 and divided by the molecular weight M of the solvent, gives a number that averages unity, or

$$100 \frac{f - f'}{f' P} \cdot \frac{m}{M} = 1.$$

We get the same result from the formula already given :

$$\frac{\Delta p}{p} m = 0.01 M,$$

which coincides with the former if only p , the pressure of the solvent, is put for f' , that of the solution, which is permissible in dealing with very dilute solutions.

On the other hand, acetic acid gave 1.61 instead of 1 when M was taken as 60, according to the formula $C_2H_4O_2$. But to do so would be to choose too small a molecular weight, for that, according to the vapour density, is 97. Taking the correct value we again get a number close to unity, as before, since

$$1.61 \times \frac{60}{97} = 1.$$

Hence, in determining the lowering of vapour pressure lies another means of measuring the molecular weight of the saturated vapour of the solvent, provided the molecular weight of the dissolved body be known.

¹ *Zeitschr. f. Phys. Chem.* 5. 423; *Berl. Ber.* 29. Ref. 941.

Accuracy attainable in measuring vapour pressures. Finally, something may be said as to carrying out the measurement of vapour pressure, and the accuracy attainable in doing so. As compared with the method of measuring the osmotic pressure directly, the vapour pressure method stands at a considerable disadvantage. The one per cent. sugar solution, that at ordinary temperatures exercises $\frac{2}{3}$ atmosphere osmotic pressure, causes a fall of only 0.4 mm. in the vapour pressure at 100°. But on the other hand, the measurement of osmotic pressure has met with such difficulties in practice, that several attempts have been made recently to obtain more accurate results by the vapour pressure method¹. An important improvement lies in increasing the difference of level which corresponds to the pressure difference to be measured. The substitution of oil for mercury (Frowein-Bremer tensimeter²) is a great advantage. But lately Smits has applied a suggestion of Kretz (Jamin, *Cours de Physique*, III, vol. iv, p. 218) in using two liquids differing but little in density. One—the heavier—was aniline, which, when moist, has at 20° the density

$$s_a = 1.022;$$

the other was water, whose density at 20° is

$$s_b = 0.998.$$

The heavier liquid occupies the lower part of the narrow tube AB (Fig. 9); the water, for the most part, the reservoirs c and d (and is covered with a thin layer of oil, not shown in the diagram, to prevent evaporation). Then suppose an

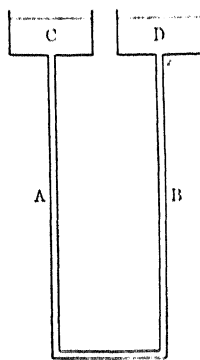


Fig. 9.

¹ Dieterici, *Wied. Ann.* 62. 617; Smits, *Arch. Néerl.* 1897; Boldingh, *Maandbl. voor Natuurk.* 21. 181.

² *Zeitschr. f. Phys. Chem.* 1. 424.

increase of pressure of p mm. of mercury applied on the right-hand side, and let h be the difference in level of the aniline produced, a the ratio of the cross section of the reservoir to that of the tube, so that $\frac{h}{a}$ is the difference in level produced in the reservoirs, then

$$13.56 p = h (1.022 + 0.948) + \frac{h}{a} 0.948,$$

so that if a is very large

$$13.56 p = 2.024 h$$

or

$$h = 6.54 p$$

i.e. in the most favourable case 1 mm. of mercury will make 6.5 mm. difference in level.

With such apparatus the following result was obtained for cane sugar ($C_{12}H_{22}O_{11}$):

7.31198 grams in 1000 grams of water gave at 25° for which $p = 4.62$ mm., a value of $\Delta p = 0.00178$ mm.

If we determine the molecular weight of sugar from these data we get:

$$\frac{\Delta p}{p} = \frac{n}{N} \text{ and } \frac{p a}{18 N} = \frac{7.31198}{1000},$$

so that

$$\frac{0.00178}{4.62} = \frac{7.31198}{1000} \cdot \frac{18}{x} \text{ and } x = \frac{7.31198 \times 18 \times 4.62}{1.78} = 342$$

in exact agreement with the formula $C_{12}H_{22}O_{11}$.

Molecular weight determination by lowering of solubility. As previously remarked, every means of separation between solvent and dissolved body implies a possible measurement of molecular weight. If the separation is effected by evaporation, then if the solvent alone is volatile we arrive at the law already given; if on the other hand only the dissolved body is volatile i.e. a gas—then

a decision as to its molecular weight may be based on Henry's law. But the separation may also be accomplished by the addition of a liquid which does not mix with the solution. Again two methods arise, according as we deal with the solvent or dissolved body passing over into the new liquid. In the first case we may expect the analogue of the law of diminution of vapour pressure, in the second that of Henry's law.

Let us take first the lowering of solubility, which was first applied to determine molecular weights by Nernst¹, and afterwards carried out in a very simple manner by Tolloczko². The whole measurement of molecular weight could be carried out in a flask (Fig. 10) of volume about 180 c.c. with a long narrow neck (1 cm. = 0.4385 c.c.; content 13 c.c.) divided in half millimetres. As liquids, ether and water were chosen, and the decrease of solubility of ether in water brought about by any substance soluble in ether measured.



Fig. 10.

To take an experiment in detail: a known quantity of water saturated with ether at 18.3° was used, containing, according to a previous measurement of solubility, 10.762 grams ether. This quantity of ether saturated with water would occupy 34.967 scale divisions of the neck. The ethereal layer occupied 4.86 scale divisions, and so weighed 1.4958 grams; on addition of 0.0952 gram benzene it increased to 6.11, equivalent to 1.88 grams.

As previously for the vapour pressure we get the formula

$$\frac{\Delta p}{p} = \frac{n}{N},$$

in which p and Δp are the pressure and decrease of pressure respectively, n and N the number of dissolved and dissolving molecules (the latter calculated from the

¹ *Zeitschr. f. Phys. Chem.* 6. 1.

² *l. c.* 20. 389.

molecular weight obtaining in the saturated vapour), so now we have

$$\frac{\Delta s}{s} = \frac{n}{N},$$

where s and Δs are the solubility and decrease of solubility respectively, n and N the number of dissolved and dissolving molecules (the latter calculated from the molecular weight obtaining in saturated solution, here therefore 74, the molecular weight that ether gives in saturated aqueous solution). Thus

$$\Delta s : s = (6.11 - 4.86) : 34.967 = 0.0358$$

$$n : N = \frac{0.0952}{x} : \frac{1.88}{74 (= C_4H_{10}O)} = 0.0358.$$

The value of x (molecular weight of benzene) so found would be nearer to the expected value if we took into account the solubility of water in ether, and the alteration in that solubility brought about by addition of benzene. Thus at the temperature of the experiment some 11 molecules of water are dissolved in 100 of ether.

On this account the so-called molecular displacement

$$\frac{\Delta s}{g} m = C$$

should be determined by means of a body of known molecular weight, and for a given mass of water and temperature, g being the mass of substance dissolved always in the same mass of ether. Then a molecular weight desired may be deduced from the value of C .

Example: 0.0655 gram of benzene effected a displacement of 0.45 cm.; the molecular weight of benzene is 78 (C_6H_6), so that

$$C = 78 \times \frac{0.45}{0.0655} = 536.$$

Then 0.1266 gram of naphthalene was taken, giving the

displacement 0.55 cm., and hence for the molecular weight of naphthalene

$$536 = x \times \frac{0.55}{0.1266},$$

$$x = 123$$

which for practical purposes agrees sufficiently with the formula $C_{10}H_8 = 128$.

Ratio of partition. As remarked on p. 43 a measurement of molecular weight may be based on the ratio of partition, and the law with regard to this may be most simply arrived at by considering the equilibrium of the vapour of the dissolved body, the mutual solubility of the two liquids being neglected. If the molecular weights in the vapour and in the two liquid phases be m , $(m)_{n_1}$, and $(m)_{n_2}$ respectively, and the concentrations c , c_1 , c_2 , then on the one hand

$$\frac{c^{n_1}}{c_1} = k_1,$$

and on the other

$$\frac{c^{n_2}}{c_2} = k_2,$$

so that

$$\frac{c^{n_2}}{c_2} = \frac{k_2^{n_1}}{k_1^{n_2}} = k \text{ and } \left(\frac{c_1}{C_1}\right)^{n_2} = \left(\frac{c_2}{C_2}\right)^{n_1},$$

where c_1 , c_2 , C_1 , C_2 are the concentrations as found in two experiments.

Hence if n_1 is known, i. e. the molecular magnitude in one liquid, then two measurements of partition will give n_2 , the magnitude in the other solvent.

As a rule the molecular magnitude is the same in both solvents, being simple in each, and so we have

$$n_1 = n_2 \text{ and } \frac{c_1}{c_2} = k,$$

i. e. constant ratio of partition, as found in certain cases by Berthelot and Jungfleisch¹. But as hydroxylic substances

¹ *Ann. de Chim. et de Phys.* (4) 26. 396, 408.

in hydroxyl-free solvents mostly occur with double molecular magnitude (p. 60) an inconstant ratio of partition is found, e. g. for acetic acid in water and benzene¹:

c_1 (gm. acetic acid in 31.5 gm. benzene)	c_2 (gm. acetic acid in 5.075 gm. water)	$\frac{c_2}{c_1}$	$\frac{c_2^2}{c_1}$
0.043	0.245	5.7	1.4
0.071	0.314	4.4	1.39
0.094	0.375	4	1.49
0.149	0.5	3.4	1.67

The fair agreement of the values of $\frac{c_2^2}{c_1}$ as compared with the decided falling off in the values of $\frac{c_2}{c_1}$ agrees with the conclusion arrived at also from other sources, that acetic acid in water exists as $C_2H_4O_2$, but in benzene practically as $(C_2H_4O_2)_2$.

(b) *The Cyclic Process cannot be carried out at Constant Temperature.*

Whilst in the foregoing methods the underlying cyclic process can be carried out at constant temperature, we have now to consider methods in which that is not the case.

Molecular weight determination by lowering of the freezing point. Separation of the solvent in the solid state, i. e. freezing of the solution, affords, as is well known, the oldest method for molecular weight measurement, which was developed on an empirical basis by Raoult before the theory of solutions was established.

The cyclic process which again leads to the rule to be applied, cannot be carried out at constant temperature, and so involves the use of the second law of thermo-dynamics. The solution is to be cooled by Δt below the freezing point of the solvent (T absolute), and at that temperature a certain quantity of ice separated, a process which can be

¹ Nernst, *Zeitschr. f. Phys. Chem.* 6. 121.

effected at the constant temperature $T - \Delta t$ if the mass of solution is so great that the separation in question makes but an inappreciable change in the concentration. Then the solution and solid solvent are to be separated and warmed to T , the solvent melted and mixed with the solution in an osmotic reversible manner (with cylinder, piston, and semipermeable membrane), a certain amount of work being gained. If Δt is very small (dt) a quantity of heat Q has in the cyclic process fallen in temperature by Δt , which implies a production of work

$$Q \frac{\Delta t}{T}.$$

If the solution contains a per cent. and so much of the solvent is frozen out as contains one kilogram-molecule m of the dissolved body, i.e. $\frac{100m}{a}$, then

$$Q = \frac{100m}{a} W,$$

where W is the latent heat of fusion of the solvent per kilogram. The work gained is, according to the previous argument,

$$APV = 2T,$$

so that

$$2T = \frac{100m}{a} W \frac{\Delta t}{T}$$

or

$$\frac{\Delta t}{a} m = \frac{0.02 T^2}{W}.$$

Here, however, the first term is the so-called molecular lowering of the freezing point t , i.e. the lowering for a one per cent. solution $\frac{\Delta t}{a}$, multiplied by the molecular weight m .

Thus for water, from $T = 273$ and $W = 80$ we may calculate

$$t = 18.6$$

(18.5 if instead of $2T$ the more exact value $1.98T$ taken), so that a one per cent. solution of methyl alcohol ($\text{CH}_3\text{OH} = 32$) would show a melting point $x = 0.5$ below zero, since

$$x \times 32 = 18.6 \text{ or } x = 0.58.$$

Vice versa, from a known depression of the freezing point the molecular weight may be calculated, and since determining molecular weights the choice always rests between values differing widely from one another, unambiguous results may be obtained by the use of the process worked out by Beckmann and Eykman. If, however, the object is to test strictly the formula deduced above, measurement of the freezing point is found to be not altogether easy. Sugar again has been the subject of many experiments, and the following table shows that of late years has satisfactory agreement been reached:—

1885 Raoult ¹	18.5	(1 per cent.)
1886 Raoult ²	25.9	(very dilute)
1888 Arrhenius ³	20.4	(1½ per cent.)
1893 Loomis ⁴	17.1	(¼ per cent.)
1893 Jones ⁵	23.7	(0.08 per cent.)
1894 Ponsot ⁶	18.77	(infinitely dilute)
1896 Abegg ⁷	18.6	(infinitely dilute)
1897 Wildermann ⁸	18.7	(0.17 per cent.)
1897 Raoult ⁹	18.72	(very dilute)

It is especially noteworthy that Raoult, in 1897, withholds the opinion expressed by him in 1885 in favour of abnormally great depression for sugar in very dilute solution and so fell into line with the theory of solutions.

It should always be remembered that the formula

$$\frac{\Delta t}{a} m = \frac{0.02 T^2}{W}$$

¹ *Compt. Rend.* 94. 1517.

² *Zeitschr. f. Phys. Chem.* 2. 497.

³ *Zeitschr. f. Phys. Chem.* 12. 642.

⁴ *Zeitschr. f. Phys. Chem.* 20. 230.

⁵ *Ann. de Chim. et de Phys.* (7) 10. 79.

⁶ *Ann. de Chim. et de Phys.* (6) 8

⁷ *Berl. Ber.* 26. 800.

⁸ *Compt. Rend.* 118. 977.

⁹ *Journ. Chem. Soc. Trans.* 1897, 1

is only strictly true for infinite dilution, so that the form

$$\frac{dt}{da} m = \frac{0.02 T^2}{W} \quad \text{or} \quad \frac{0.0198 T^2}{W}.$$

is to be preferred, where da is the dissolved substance in 100 parts.

Molecular weight determination by the rise of boiling point. Just as the solvent can be removed by freezing, so it can be separated from the dissolved body by boiling, and the lowering of vapour pressure already dealt with corresponds to a rise in the boiling point. This may be determined in magnitude by means of a cyclic process similar to that referring to the freezing point, and amounts to

$$t = \frac{0.02 T^2}{W} \quad \text{or exactly} \quad \frac{0.0198 T^2}{W},$$

where t is the molecular rise of boiling point (i. e. $\frac{dt}{da} m$, p. 56), T the absolute temperature of the boiling point, W the latent heat of evaporation. The method of molecular weight determinations based on this has also been worked out by Beckmann. It is usually not so good as the freezing-point method, because the molecular rise of boiling point is, on account of the great latent heat of evaporation, relatively small.

This will be plain from the following table, which gives the freezing point (Fp), latent heat of fusion (W_f), boiling point (Sp), and latent heat of evaporation at the boiling point (W_s), together with the molecular change in freezing point (M_f), and boiling point (M_s), calculated from the formula

$$M = \frac{0.0198 T^2}{W}.$$

Substance.	Fp	W_f	M_f	Sp	W_s	M_s
Water . . .	0°	80	18.5	100°	536	5.14
Acetic acid . .	17°	44	37.8	118°	85	35.6
Benzene . . .	3°	30	50.3	80°	93	33.4

It may be added that recently the boiling-point method has been applied in a simpler form by Landsberger¹ and Walker², by passing e.g. ether vapour, generated in a flask, through the ethereal solution of the substance investigated, till the thermometer no longer rises, and indicates the boiling point of the solution.

*Molecular weight determination by means of the change of solubility with temperature*³. If no third substance is employed to effect the separation between dissolved body and solvent, and we omit that in the list of methods, it is in the first place difference in state of aggregation which allows of the separation. Thus molecular weight determination by means of vapour pressure and boiling point is possible on account of the separation of solvent as vapour; determination by means of the absorption coefficient is possible on account of the separation of the dissolved body as gas. Separation of the solvent in the solid form leads to the method of the lowering of the freezing point, and finally the account may be completed with the possibility of separating the dissolved body in the solid form. The method so indicated may now be taken.

The method is similar to that applied on p. 21 to gas and vapours, involving the well-known formula

$$AVdP = q \frac{dT}{T}.$$

Here V is the increase of volume due to evaporation of a definite quantity, and q , the heat absorbed, refers to the same.

With regard to solutions this equation may be transformed, according to Part I, p. 36, into

$$\frac{d \log C}{dT} = \frac{Q}{2T^2} \text{ or } \frac{dC}{C dT} = \frac{Q}{2T^2},$$

¹ Berl. Ber. 31, 458.

² Journ. Chem. Soc., 73, 502.

³ Verschaffelt, *Zeitschr. f. Phys. Chem.* 15, 449; Van Laar, *l.c.* 15, 473; 17, 545; 27, 337; Goldschmidt, *l.c.* 17, 145; 25, 91; Noyes, *l.c.* 26, 699.

in which Q is the heat absorbed on solution of one kilogram-molecule, C the concentration.

This formula allows of a molecular weight determination of the dissolved substance, by calculating L from the data on solubility, and dividing by the observed heat of solution per kilogram; thus for succinic acid ($C_4H_6O_4$) the amounts dissolved in 100 parts of water at 0° and 8.5° respectively are 2.88 and 4.22; hence we get from

$$\frac{\Delta C}{C \Delta T} = \frac{Q}{2 T^2}$$

$$Q = \frac{2 T^2 \Delta C}{C \Delta T} = \frac{2 \times 277.25^2}{3.55 \times 8.5} = 6830.$$

The heat of solution per kilogram is 55, and therefore the molecular weight $\frac{6830}{55} = 124$ ($C_4H_6O_4 = 118$).

C. Results.

1. *Simple Molecular Magnitude of Dissolved Bodies.*

Putting together the results of the numerous determinations of the molecular weights of dissolved bodies, the leading conclusion arrived at appears to be that the molecular magnitude is usually that corresponding to the simplest formula that answers to the quantitative composition, and the chemical relations of formation and transformation. This conclusion has helped not a little towards the favourable reception of the theory of solutions, and to the working out of the molecular weight methods based on it.

Larger molecules. Agreement with the results of gas density measurements. In the first place, departures from the simplest possible molecular formula are found in cases in which the gas density indicates the same thing. The molecular magnitude of the elements, already referred to, may be mentioned in this regard. Most are diatomic: so also are oxygen, nitrogen, and hydrogen in aqueous solution,

since Henry's law of absorption applies to them (p. 31); for iodine the same has been shown by measurements of the freezing point¹. Again, the monatomicity of the metals (p. 25), deduced from their vapour densities, is found to be true for solution in mercury², whilst phosphorus and sulphur appear as tetr- and oct-atomic respectively, as in the form of vapour.

Researches on the molecular weights of the elements can thus be carried much further, since the non-volatility of the metals is here of no consequence, and so nearly all the metals have been studied in solution in tin, and have mostly proved monatomic.

As to compounds, the tendency of acetic and formic acids to form double molecules, shown by the vapour density, recurs in many (hydroxyl-free) solvents³.

Larger molecules in hydroxylic compounds. What does not appear from the investigation of gases and vapours is the tendency of nearly all hydroxylic compounds to form double molecules when in somewhat concentrated solution, as was mentioned for formic and acetic acids. This is found to be the case in general for organic acids, for the alcohols, and for water. The presence of double molecules, however, depends on the solvent, being found only in hydroxyl-free liquids, such as the hydrocarbons, chloroform, and carbon disulphide. In hydroxylic solvents, phenol, acetic acid, water, the reduplication does not appear, either because of a dissociating action of the solvent, or because the dissolved body forms molecular complexes with the solvent, in which only one molecule of dissolved occurs. Hence in practice, as the smallest molecular weight answering to the chemical behaviour is sought, it appears that hydroxylic solvents such as acetic acid are to be preferred, especially when dealing with hydroxylic bodies.

¹ Beckmann, *Zeitschr. f. Phys. Chem.* 5. 76; 17. 107; 22. 614; Helff, l. c. 12. 219; Aronstein and Meihuizen, *Verh. Kon. Akad.* Amsterdam, 1898.

² Ramsay, *Zeitschr. f. Phys. Chem.* 3. 359; Tammann, l. c. 3. 441.

³ Beckmann, l. c. 2. 742.

2. *Development of the Stereochemical Conceptions.*

Molecularweight measurements play a specially important part in studying the cause of the isomerism between two bodies of the same composition. For it is then possible to decide whether there is a difference in molecular magnitude, i.e. polymerism, or a difference in construction between two molecules of the same size, i.e. isomerism in the narrower sense. It may be remarked here, that with regard to the development of stereo-isomerism, which is a special kind of isomerism attributed to the arrangement of the molecule in space, molecular weight determinations form an indispensable aid, since it is necessary first to prove that differences between equally composed molecules are in question. Hence it was a fortunate coincidence that just at the time the theory of stereochemistry was discovered, the new methods for the measurement of molecular weights in solution, based on the theory of solutions, were introduced. The interesting cases of isomerism in the truxillic acids, the benzoinoximes, and many other compounds important for stereochemistry, could hardly have been so quickly and certainly brought into light without the new methods for molecular weight determination.

3. *Abnormal Results for Isomorphous Compounds.*

A very striking exception appears when a substance is dissolved in another isomorphous with it, as thiophene in benzene. The lowering of the freezing point is then decidedly less; in the case mentioned only about two-thirds of the normal amount. In such cases, as has actually been shown¹, the dissolved substance separates out in an isomorphous mixture with the solvent when the latter

¹ Van Bylert, *Zeitschr. f. Phys. Chem.* 8. 343; Beckmann, l.c. 17. 107; 22. 609.

freezes; hence we have a departure from the assumptions made in determining the formula

$$\frac{0.02 T^2}{W},$$

and it will appear later that for that reason the lowering of the freezing point should be smaller.

The phenomenon in question has been applied by Ciamician and Garelli¹ to settle doubtful cases of isomorphism, and by that means the constitutional formula, since it is known that isomorphism goes hand in hand with similarity of constitution.

4. *Abnormal Results for Electrolytes.*

Lastly we must consider the great exceptions which occur in electrolytes, i.e. especially solutions of salts, strong acids, and bases in water, where the lowering of the freezing point often amounts to twice or more times the normal amount². It was just this phenomenon that so long stood in the way of the discovery of the simple laws applicable to dilute solutions, which first came to light when Raoult made his freezing-point measurements on non-electrolytic solutions, i.e. on solutions in solvents other than water, and solutions in water of organic substances not of a salt character. It is well known that the phenomenon in question led to the theory of electrolytic dissociation, which now requires special treatment.

The Theory of Electrolytic Dissociation. Arrhenius attributed the abnormally large change of freezing point just mentioned, and the abnormally high osmotic pressure deduced from it, to a decomposition into ions, i.e. electrically charged portions of molecules. The extensive data

¹ *Zeitschr. f. Phys. Chem.* 13. 1, 18. 51, 21. 1.

² The greatest deviation has lately been found by Crum Brown for the salts of sex-basic mellitic acid.

accumulated in support of this view will only be partly mentioned here. In the Third Part of these lectures, in which the relations between constitution and properties are to be discussed, many opportunities will arise to draw qualitative and quantitative conclusions from the idea of Arrhenius, as was the case in the First Part (p. 117), in dealing with the conditions of equilibrium in electrolytes. Here we are specially concerned with the question, on which the decisive proof turns, whether the degree of decomposition deduced from the theory of solutions agrees with that arrived at independently on the basis of the electrolytic dissociation theory.

The form in which the departure of electrolytes from Avogadro's law, as applied to solutions, is to be given, may conveniently follow on the so-called isotonic coefficients introduced by de Vries (p. 38); these give how many times more effective a molecule of salt in an isotonic solution is, with regard to plasmolytic or osmotic action, than a sugar molecule, the latter being, for special reasons, taken as 2. We have modified this mode of expression by taking sugar and other substances following Avogadro's law as unity, and writing the halved isotonic coefficients so arrived at with the letter ι . If then, for a certain concentration, $\iota = 1.75$ for nitre, that means that if each molecule of nitre were replaced by 1.75 molecules of sugar, a solution isotonic with that of nitre would be obtained. Hence the osmotic pressure of the nitre solution is 1.75 times the normal amount, so that the quantity ι may also be obtained as the ratio between the molecular depression of the freezing point t proportional to the osmotic pressure, and the normal value 18.5 found for sugar and other non-electrolytes, or

$$\iota = \frac{t}{18.5}.$$

For the same temperature and concentration, the same value of ι should be obtained, whichever of the methods

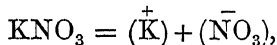
already mentioned is adopted—whether based on the law of absorption, on the freezing point, or on direct measurement of osmotic pressure; and the confirmation that Arrhenius' conception has received lies in the agreement between the value of ι so obtained and that independently reached on the basis of that conception.

In the first place then we must consider the relation between ι and the conductivity.

Electrolytes have, it is known, a conductivity which, referred always to the same—say normal—concentration, increases with increasing dilution. Calling this the molecular conductivity μ —the conductivity of mercury at 0° being taken as unity, and the number multiplied by 10^7 for convenience—we have for KNO_3 at 18° , according to Kohlrausch:

Normality =	3	1	$\frac{1}{2}$	$\frac{1}{10}$	$\frac{1}{20}$	$\frac{1}{33.3}$	$\frac{1}{100}$
μ	= 57.2	75.2	88.9	103.7	106.7	112.2	114
Normality =	$\frac{1}{166.7}$	$\frac{1}{500}$	$\frac{1}{1000}$	$\frac{1}{1667}$	$\frac{1}{5000}$	$\frac{1}{10000}$	$\frac{1}{16667}$
μ	= 117.3	118	119	119.9	120.7	122	119.8

i.e. a number which increases asymptotically as the dilution becomes greater. The explanation of this fact on Arrhenius' theory is that with the dilution comes an increasing ionic decomposition according to the equation



where $(\overset{+}{\text{K}})$ and $(\overset{-}{\text{NO}_3})$ represent the positively and negatively charged ions respectively. This decomposition is practically complete for the limiting value

$$\mu_\infty = 122.$$

Theoretically it would only be reached on infinite dilution, and is therefore represented by μ_∞ .

If the conductivity depends, as we have assumed, only on the ions present, the quotient

$$\alpha = \frac{\mu}{\mu_\infty}$$

represents the fraction decomposed, and the total number of molecules, counting each ion as such, exceeds the normal amount in the ratio

$$1 : (1 - \alpha) + 2 \alpha = 1 : 1 + \alpha,$$

so that we have

$$\iota = 1 + \alpha = 1 + \frac{\mu}{\mu_{\infty}}.$$

Comparing a special case directly with de Vries' experiments in which urea was chosen as normal substance, we find for the concentrations mentioned the following results (plasmolysis p , no plasmolysis n , intermediate state np):

Normality	Urea					Nitre				
N	≈ 0.285	0.3	0.315	0.33	0.345	$N = 0.16$	0.17	0.18	0.19	0.20
	n	n	np	p	p	n	n	np	p	p

so that 0.315 normal urea is isotonic with 0.18 normal nitre. Accordingly for a 0.18 normal nitre solution

$$\iota = \frac{0.315}{0.18} = 1.75.$$

By the conductivity we get, interpolating for the same solution,

$$\mu = 99.7, \text{ so that } \iota = 1 + \frac{\mu}{\mu_{\infty}} = 1 + \frac{99.7}{1.22} = 1.81.$$

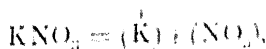
The agreement is here satisfactory. Unfortunately it has not in all cases remained equally so on application of the more exact procedure of the freezing point.

It would be very desirable to form a collection of results obtained by the freezing-point method, to serve as a test of Arrhenius' law by comparison with the collection of data on conductivity¹.

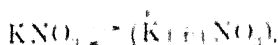
Under these circumstances it seems desirable to choose Ostwald's 'law of dilution' as a second characteristic, and divide electrolytes into two groups according as they follow it or not.

¹ Das Leitvermögen der Elektrolyte, insbesondere der Lösungen, Kohlrausch and Holborn. Leipzig, 1898.

Electrolytes which follow Ostwald's law of dilution. For a dissociation in a dissolved electrolyte in the sense of the equation



i.e. an equilibrium symbolized by



if the ions are treated as molecules it seems an inevitable consequence of the equation of equilibria already arrived at,

$$\Sigma n \log C^i = \text{const.},$$

that

$$\log C_{(\text{NO}_3)}^i + \log C_{(\text{K})}^i - \log C_{\text{KNO}_3}^i = \text{const.},$$

the concentration of the two systems being taken with opposite signs; this may be written

$$\frac{C_{(\text{NO}_3)}^i C_{(\text{K})}^i}{C_{\text{KNO}_3}^i} = K,$$

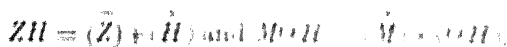
or if V be the volume in litres of *one* gram-molecule (reciprocal of the normality),

$$C_{\text{KNO}_3} = \frac{1-u}{V} \cdot C_{(\text{NO}_3)} = C_{(\text{K})} = \frac{u}{V} \cdot u = \frac{u^2}{\mu_+},$$

whence

$$(1-u)^2 V = K \text{ or } \frac{u^2}{\mu_+(\mu_+ - u)} V = K.$$

However, for salts, e.g. nitre, this relation does not hold, as we shall see later, but only for a definite though very numerous group of electrolytes, viz. acids and bases in aqueous solution, that decompose in the manner



and of these only the weak acids and bases. The law seems to be restricted to cases in which the dissociation yields ions of the solvent water, and then only when their concentration is small.

As an example, the data for chloracetic acid at 14° are as follows ¹, the calculated values of $\frac{\mu}{\mu_{\infty}}$ being derived from the equation

$$\frac{\mu^2}{\mu_{\infty}(\mu_{\infty} - \mu)} V = K.$$

V	μ	$\frac{\mu}{\mu_{\infty}}$ obs.	$\frac{\mu}{\mu_{\infty}}$ calc. from $\log K = 7.2 - 10$
20	51.6	0.166	0.163
205	132	0.423	0.43
408	170	0.547	0.543
2060	251	0.806	0.801
4080	274	0.881	0.88
10100	295	0.948	0.944
20700	300	0.963	0.971
∞	311	1	1

Clearly here the decomposition as measured electrically follows the course anticipated on the theory of dissociation. Accordingly we find, e. g. for dichloracetic acid, which also follows Ostwald's law, that the values of i obtained from the molecular depression of the freezing point (t_M), and those from the conductivity, agree ².

Normality	$i = \frac{t_M}{18.7}$	$i = 1 + \frac{\mu}{\mu_{\infty}}$
0.002599	1.966	1.956
0.005177	1.911	1.913
0.01033	1.852	1.843
0.01447	1.763	1.806
0.02048	1.717	1.731
0.02778	1.69	1.703

The agreement is satisfactory, and might well be complete if we remember that the freezing-point measurement—always the more difficult—refers to 0°, while the electrical is for 18°.

Electrolytes which do not follow Ostwald's law of dilution.
The case is quite different for salts and strong acids and

¹ Van 't Hoff and Reicher, *Zeitschr. f. Phys. Chem.* 2. 781.

² Wildermann, l. c. 19. 242.

bases. If, e. g., we take the former value of the conductivity of nitre, and calculate

$$\log \frac{\mu^2}{\mu_\infty (\mu_\infty - \mu) V},$$

where V is the reciprocal of the normality and $\mu_\infty = 122$, we get:

Normality (N) =	3	1	$\frac{1}{2}$	$\frac{1}{10}$	$\frac{1}{20}$	$\frac{1}{33.3}$	$\frac{1}{100}$
$\mu =$	57.2	75.2	83.9	103.7	106.7	112.2	114
$\log \frac{\mu^2 N}{122 - \mu} =$	2.1939	2.081	1.9657	1.7689	1.5707	1.5864	1.2107

Normality (N) =	$\frac{1}{166.7}$	$\frac{1}{500}$	$\frac{1}{1000}$	$\frac{1}{1667}$	$\frac{1}{5000}$		
$\mu =$	117.3	118	119	119.9	120.7		
$\log \frac{\mu^2 N}{122 - \mu} =$	1.2446	0.8427	0.6739	0.6037	0.3503		

The relation suggested by Rudolphi and van't Hoff¹,

$$\frac{\alpha^3}{(1 - \alpha^2) V} = K, \quad \alpha = \frac{\mu}{\mu_\infty},$$

does not remove this difficulty in principle, for though it certainly agrees better with the facts (Part I, p. 124) it has no necessary basis, and so can at present only be regarded as empirical.

Moreover, there is a considerable difference between the values found for the dissociated part² (in per cent.), e. g., for sodium chloride, by the freezing-point method by Jones, Loomis, Abegg, Raoult, and from the conductivity by Kohlrausch:

POTASSIUM CHLORIDE.					
N	Jones	Loomis	Abegg	Raoult	Kohlrausch
0.01	95	95	96	—	94.5
0.03	92	90	90	91	91.1
0.05	90	89	88	88	89.1
0.1	87	86	—	85	86.2

SODIUM CHLORIDE.					
N	Jones	Loomis	Abegg	Raoult	Kohlrausch
0.01	95	99	105	—	93.7
0.03	92	93	92	97	89.6
0.05	90	91	92	93	87.3
0.1	88	88	88	89	84.2

¹ *Zeitschr. f. Phys. Chem.* 17, 385, 18, 305; Kohlrausch, l. c. 18, 661.

² Noyes, l. c. 26, 709.

Evidently, then, dissolved salts, strong acids and bases, must be treated with caution as electrolytes, for though there is undoubtedly dissociation, and the assumption of dissociation into ions appears to be indispensable, yet the exact amount of that dissociation, and the mechanism of it, are insufficiently explained. In these cases it is necessary to hold by the thermo-dynamic relations based on vapour and osmotic pressures, &c., and to treat the calculations made from conductivity data as rough estimates, whose exact value is yet to be determined, although the commonly close agreement indicates a most valuable conclusion, as will appear better in the Third Part.

It is otherwise as regards high dilutions, at which, especially for strong monobasic acids, monacid bases, and their salts, the dissociation found osmotically and electrically is practically complete, and so ignorance of the law of dissociation does not stand in the way; calculations then, with the assumption of complete dissociation, recover strict applicability.

To give a notion of the case, we quote the degrees of dissociation found for decinormal solutions at 18° from conductivity measurements:

Strong monobasic acids and monacid bases:

HCl 94% KOH 93% NaOH 90%.

Salts of the above acids and bases:

KCl 86% KNO₃ 85% NaCl 84% NaNO₃ 84%.

Salts of strong dibasic acids or diacid bases:

Na₂SO₄ 69% BaCl₂ 75%.

Salts of dibasic acids and diacid bases:

MgSO₄ 45% CuSO₄ 39%.

Already in the copper salt we are dealing with a weak base; if further a weak acid be chosen, as in copper acetate, the ionization is further reduced; then, however, quite a different dissociation appears—the hydrolytic—which results in formation of free acetic acid and free base or basic salt, an effect that does not come into consideration with the salts mentioned above.

§ 3. SOLID SOLUTIONS¹.

There seems a prospect of extending the theory of solutions which allows of determining molecular weight in solution, to homogeneous solid mixtures. This possibility is conveyed by the expression 'solid solution' for such homogeneous mixtures.

According to the data which are at present available for testing this assumption, it seems necessary to distinguish between amorphous 'solid solutions,' such as e.g. the glasses which are homogeneous mixtures of silicates, and 'isomorphous mixtures.' The latter are further removed from solutions just on account of their crystalline structure, whilst for the glasses there is a continuous series of states connecting the solid and liquid conditions that almost excludes any limit to the applicability of the laws of solution. Only the equilibrium reached by diffusion takes more and more time to reach on account of the increasing viscosity, and consequently the difficult problem in the study of such solid solutions lies in the establishment of the necessary equilibrium.

Qualitatively these solid solutions, both crystalline and amorphous, have much in common with liquid solutions, but on the quantitative side of the problem it is necessary first to keep to amorphous, or occasionally crystalline solid solutions, whilst isomorphous mixtures in the narrower senses will be discussed in the third division under molecular structure.

First, a few leading traits of a qualitative character may be touched upon¹.

A. Qualitative Considerations.

As regards qualitative features, first come the experiments on the lowering of vapour pressure of solids when

¹ Bodländer, *Neues Jahrbuch f. Mineralogie, Geologie, Paläontologie*, 1898.

² Van 't Hoff, *Zeitschr. f. Phys. Chem.* 5. 322.

others form with them homogeneous or isomorphous mixtures. Von Hauer and Lehmann observed in this respect that the tendency of hydrated salts to effloresce, which indicates a somewhat high vapour pressure, is reduced by isomorphous mixture; this was observed for lead sulphite in mixture with the corresponding calcium and strontium salts, iron alum with aluminium alum, copper formate with the formates of barium and strontium. The essential point is that each component shows a greater tendency to effloresce than the compound.

This reduction in saturation pressure corresponds to the observation already mentioned (p. 61), that when the dissolved substance separates out along with the solvent as an isomorphous mixture,

the depression is abnormally small. Thus e.g. in Fig. 11 let AB and BC be the vapour pressures of the solid and liquid solvent respectively, so that B, their point of intersection, represents the melting point T_1 . If now the solution, by taking up any non-volatile body, comes to have the smaller vapour pressure B_2C_2 , the depression produced is T_2T_1 ;

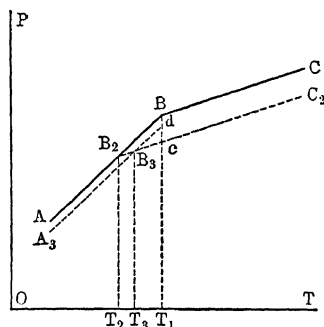


Fig. 11.

if, however, the solid solvent also takes up some of the dissolved body, and so possesses the smaller vapour pressure A_3B_3 , the depression is also less, viz. T_3T_1 , always on the assumption that the freezing point is the temperature at which solid and liquid have the same vapour pressure, which is certainly the case when the dissolved body is non-volatile.

It may be remarked that just on this account the treatment of isomorphous mixtures is less simple. The close relation of the two bodies, as benzene and thiophene¹,

¹ Van Bylert, *Zeitschr. f. Phys. Chem.* 8. 343.

naphthol and naphthalene¹, chlorobromo- and iodoform², &c., excludes at once the assumption that only one body, that present in great excess, the so-called solvent, is volatile. The condition of equilibrium at the freezing point is then no longer merely equality in the partial pressures of the solvent in the solid and liquid conditions; only if the same equality of pressure holds for the dissolved substance do the conditions suffice for equilibrium. The question arises whether the fixed composition thus arrived at for the isomorphous mixture separating from a solution of given composition agrees with the facts, or, in other words, whether the cause that produces mixed crystallization does not involve a factor that influences the composition of the mixture. This is probable, on the one hand, because isomorphous mixtures of all compositions cannot always be obtained (Part I, p. 55); on the other hand this may perhaps correspond to a simultaneous formation of two layers in the liquid. The whole thing awaits further investigation.

Another point that may be added in considering the qualitative relations is that the diminution in vapour pressure which a solid suffers when a non-volatile body is taken up by it, involves a diminution of solubility, so that e. g. an isomorphous mixture should separate out when saturated solutions of alum and iron-alum are mixed.

B. Quantitative Results.

As regards the quantitative side of the problem the experimental data are not yet very complete or conclusive. The important common result that workers in this field have so far arrived at is that the solid state is not distinguished by a more complex molecular structure, but that in solids, too, the dissolved molecule has as a rule the smallest size compatible with chemical facts, and at most double that size, as was found to be the case in liquid solutions. This result would be particularly important for isomorphous

¹ Küster, *Zeitschr. f. Phys. Chem.* 13. 452, 17. 355.

² Bruni, *Atti R. Accad. dei Lincei, Roma*, 7. 166.

mixtures, because then it would be allowable to extend the conclusion from the small isomorphous admixture to the whole crystal, since in such a case all the crystalline molecules may well be assumed to have the same structure.

On considering in more detail particular experiments, it will be well to treat separately the crystalline mixtures and the amorphous solutions. In the former we have to take account of the complication due to electrolytic dissociation, while in the latter we must bear in mind that a separation of mixed material, spoken of as a solid solution, may be the result of an alternate formation of layers, i. e. something quite different from solid solution.

1. *Isomorphous Mixtures of Electrolytes.*

In the region of solid solutions, as commonly elsewhere, the most complicated cases theoretically are the most accessible to measurement, and the first attempt to elaborate a method of molecular weight determination for solids referred to just this case of isomorphous mixtures.

Nernst¹ made use of Roozeboom's² results on the composition of the mixed crystals of thallium and potassium chlorate obtained on adding a known amount of potassium chlorate solution to saturated thallium chlorate. It was found that the concentration of the undissociated potassium chlorate in solution (normality c) was nearly proportional to that of the total potassium chlorate in the mixed crystal (x in molecular percentage).

c	x	$1000 \frac{c}{x}$
0.0168	2	8.4
0.0873	12.61	6.9
0.1536	25.01	6.1

Applying the law of partition stated on p. 53, as regards the proportion of a substance in two non-miscible liquid layers, it may be concluded from this that potassium chlorate in the isomorphous mixture has the same molecular magnitude as in the solution, i. e. KClO_3 .

¹ *Zeitschr. f. Phys. Chem.* 6. 577, 9. 137.

² *l. c.* 8. 516.

Fock¹ eliminated as far as possible the influence of electrolytic dissociation by using solutions of nearly the same total concentration obtained by adding a great excess of a salt containing the same ion; so that if the electrolytes dealt with are equally strongly dissociated, the concentration of each dissociated part remains the same. In these cases the concentration in the solution (c_1 in normality) usually appeared proportional to that in the mixed crystals (x in molecular per cent.). An experiment carried out at 25° with thallium nitrate may serve as example; the solution contained the amount of potassium nitrate (c_2 in normality) necessary to keep up the total concentration.

c_1	c_2	$c_1 + c_2$	x	$\frac{c_1}{x}$
0.0089	3.2515	3.2604	0.031	0.114
0.0231	3.2851	3.3082	0.20	0.116
0.0663	3.2981	3.3644	0.57	0.116
0.1869	3.2944	3.4813	1.71	0.103
0.2309	3.1724	3.4033	2.19	0.109
0.3238	3.2658	3.5896	2.72	0.117

Here, as in most other cases, the conclusion to be drawn is in favour of simple molecular magnitude in crystals.

2. Crystalline Mixtures of Non-electrolytes.

Here we come across, on the one hand, the most striking confirmation of the conception of solid solutions, especially as shown by van Hylert, Beckmann, and Brunel, and on the other a peculiar behaviour noted by Kuster. The observed data are not sufficient to allow of characterizing the two categories with certainty; in the first case it seems as if any relation of crystalline forms, e.g. at least between iodine and solid benzene, were excluded, whilst in the latter case, e.g. between hexachlor- and pentachlorobromketopentane (C_5Cl_6O and C_5Cl_5BrO), far reaching isomerorphism is conceivable; we will, in the first place, therefore, distinguish 'crystalline solid solutions' and 'isomorphous mixtures.'

¹ *Ber. Ber.* 28, 408, 2734; 31, 166, 566; *Zentralbl. f. Chem.* 20, 317.

Crystalline solid solutions. The two cases so far studied are of iodine in benzene and thiophene in benzene¹. The benzene crystallizing out in each case is found to contain iodine or thiophene, and quantitative observations showed proportionality between the concentrations in the solid solution and liquid.

IODINE IN BENZENE.

Liquid	35.39 per cent.	2.587 per cent.	0.945 per cent.
Solid solution . .	1.279 "	0.025 "	0.317 "
Ratio	0.377 "	0.358 "	0.336 "

Mean 0.357

For thiophene the ratio only varied from 0.396 to 0.379 with the maximum intervening value 0.449 (mean 0.414) for solutions containing 1.16 to 15.91 per cent. of thiophene.

From this proportionality it may be concluded, according to p. 72, that iodine and thiophene have the same molecular weights in solid and liquid benzene, i.e. the weights corresponding to the formula I_2 and C_4H_4S .

At the same time we have a means of testing further quantitatively the considerations on the lowering of the freezing point given on p. 71. It appeared there that joint crystallization reduced the depression of the freezing point from T_2T_1 to T_3T_1 (Fig. 11). The quantitative relations are clear from the figure, viz.:

$$T_1T_3 : T_1T_2 :: cB_3 : cB_2 :: cd : cB :: cB :: dB : cB,$$

where cB and dB are the lowerings of vapour pressure suffered by the liquid and solid respectively. These, if the dissolved substance has the same molecular weight in each, are proportional to the concentrations. Hence

$$T_1T_3 = T_1T_2 \left(1 + \frac{dB}{cB}\right) = 0.643 T_1T_2 \text{ and } 0.551 T_1T_2$$

respectively for iodine and thiophene.

The molecular depressions will therefore be only 0.643

¹ Van Bylest, *Zeits. f. phys. Chem.* B, 344; Beckmann and Stock, l. c. 17, 120, 22, 600. See further Küster, l. c. 17, 304. Würffel, *Beiträge zur Molekulargewichtbestimmung in kristallinen Substanzen*, Inaug.-Diss., Marburg, 1896.

and 0.551 of the normal value 50 for iodine and thiophene. They were found:

	<i>In 100 gm. (p)</i>	<i>Depression (t)</i>	<i>Mol. lowering = $\frac{t}{p} M$</i>
Iodine ($M = 254$)	0.914	0.129	36
"	2.24	0.313	35
"	4.27	0.601	36
Thiophene ($M = 84$)	0.51	0.192	31
"	1.12	0.422	31
"	2.16	0.812	31
"	3.25	1.213	31

} instead of 32

} instead of 28

A similar confirmation is supplied by Brunni's¹ experiments on iodoform dissolved in bromoform. Here again bromoform crystallized out with the dissolved body, and the constant ratio (0.35 to 0.37) allowed of the conclusion that solid iodoform consists of HCl_3 , as in liquid solution. The molecular depression was found as 0.66 of the normal amount, while 0.65 to 0.63 was to be expected.

Isomorphous mixtures. Against this result, in all respects satisfactory, has to be set the fact, observed especially by Küster¹, that isomorphous mixtures sometimes behave quite differently as regards melting point, which may be calculated from the simple rule of mixture

$$S = a S_1 + (1 - a) S_2,$$

where S_1 , S_2 are the melting points of the components, and a , $1 - a$ the quantities (in molecules) of the two respectively. Thus for hexachlor- and pentachlorbrom-ketopentane the following results were found:—

<i>Molecules</i>		<i>Melting point</i>	<i>Melting point</i>
$\text{C}_6\text{Cl}_6\text{O} (a)$	$\text{C}_5\text{Cl}_5\text{BrO} (1 - a)$	(obs.)	(calc.)
1	0	87.5 (S_1)	—
0.9471	0.0529	87.99	88.04
0.9135	0.0865	88.3	88.38
0.8571	0.1429	88.8	88.96
0.8253	0.1747	89.11	89.28
0.7468	0.2532	89.85	90.09

¹ *Atti R. Accad. dei Lincei* (5) 7. 166.

² *Zeitschr. f. Phys. Chem.* 5. 601, 8. 577.

Molecules		Melting point	Melting point
C_5Cl_6O (a)	C_5Cl_5BrO (1-a)	(obs.)	(calc.)
0.7005	0.2005	90.3	90.55
0.5774	0.4226	91.61	91.81
0.4100	0.5801	93.27	93.51
0.2867	0.7133	94.50	94.78
0.1701	0.8209	95.74	95.88
0.0955	0.9045	96.67	96.74
0.0200	0.9800	97.49	97.50
0	1	97.71 (S ₂)	—

The same behaviour was found for some other pairs of very similar bodies. Still exceptions are found¹ which increase with the difference between the two melting points, and the abnormally large depression to be expected in the higher melting substance, when the difference of melting points is great, does not occur, e.g., with carbazol and phenanthrene. On the other hand, there is the characteristic rise of melting point, observed by Küster, e.g. for β -naphthol in naphthalene, accompanying the separation of a mixture richer in β -naphthol² in accordance with the theory of solutions. It is so far not certain that Küster's pairs of substances form any departure from the theory.

3. Amorphous Solid Solutions.

Amorphous solid solutions would well form the first subjects of experiment in this department. Küster³ has made experiments on the partition of ether between water and caoutchouc, and he concluded with considerable probability from the results, that ether in caoutchouc has the simple molecular weight when dilute, but double when more concentrated.

The choice is, however, limited by the facility amorphous solids have of taking up substances in quite another way than mixture or solution. Thus the absorption of gases and

¹ Giacelli, *Ann. Chim. Ital.* 1894, 11, 204.

² Brunni, *Ann. R. Ist. Sci. Univ. Bonn*, 1892, 2, p. 138.

³ *Zeits. für phys. Chem.* 13, 437.

dissolved bodies by animal charcoal¹, of dyes by fibres², and so on are rather to be treated as surface phenomena.

We will choose the simplest of such compounds for detailed examination—the so-called palladium hydride³. What essentially concerns us in the research is the change in the amount of hydrogen absorbed by palladium at constant temperature, when the pressure, and therefore the concentration, of the hydrogen is changed, as well as the concentration of the solution of hydrogen in palladium

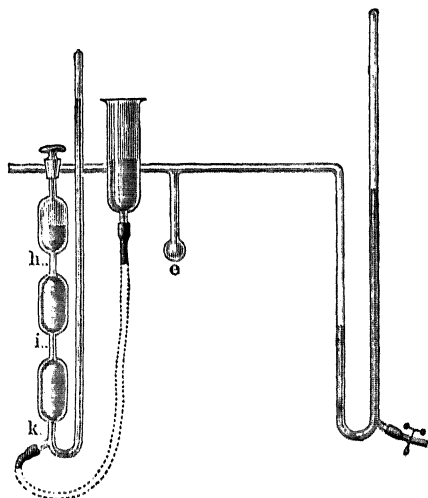


Fig. 12.

formed. The apparatus (Fig. 12) allows of bringing a known weight of palladium in *e* at definite temperature into contact with hydrogen whose pressure could be read off the manometer, whilst the quantity absorbed could be estimated from the original amount and the amount

¹ Schmidt, *Zeitschr. f. Phys. Chem.* 15. 56.

² Witt, *Farbenzeitung*, 1890-91, No. 1; Walker, Appleyard, *Journ. Chem. Soc.* 69. 1334.

³ Hoitsema, *Zeitschr. f. Phys. Chem.* 17. 1. See also Shields, *Proc. Roy. Soc. Edinb.* 1897-98, p. 169.

remaining: the quantities being calculated by means of the known volume of the apparatus (provided with marks at h, i, k) and the pressure and temperature.

It was already known, from the experiments of Troost and Hautefeuille, that the amount of hydrogen absorbed first rises with the pressure, whilst on further absorption the pressure becomes constant, which suggests the formation of a compound. We may quote the data for 150° : the pressure (P) in millimetres, the number of hydrogen atoms absorbed by one palladium (H), and the ratio between the increase of pressure (ΔP) and the quantity absorbed (ΔH):

Pressure (P)	Amount of absorption (H)	$\Delta P : \Delta H$
26.2 mm.	0.0097	—
82.8 „	0.0163	8576
165.4 „	0.023	12328
393.7 „	0.0387	14541
622.6 „	0.060	10746
757.3 „	0.083	5857
836.6 „	0.122	2933
858.5 „	0.152	730
875.5 „	0.210	254
876.3 „	0.253	24
901.7 „	0.351	259
927.6 „	0.409	446
1012.1 „	0.443	2485
1211.8 „	0.477	5874
1300.6 „	0.488	8073

Troost and Hautefeuille's opinion in favour of the formation of a compound was strengthened by the fact that at the temperature they employed the maximum hydrogen taken up in the interval of nearly constant pressure corresponded to the formula Pd_2H . It appears, however, from the newer researches discussed here, that this quantity does not represent any definite atomic ratio, and especially that it varies with the temperature.

At 10° concentration about $\text{PdH}_{0.66}$
 „ 180° „ „ $\text{PdH}_{0.37}$.

The possible explanation of these facts is that at constant pressure two solid solutions are present in the palladium,

which behave like two liquid layers¹. Thus e.g. a similar behaviour as regards pressure would be found if unsaturated ether vapour were compressed in contact with water. At first the pressure will rise, with increasing absorption of ether by the water; then a second layer will be formed, very rich in ether, i.e. moist ether, and then the pressure will remain constant whilst the new layer increases in bulk at the cost of the old. When the latter has vanished the pressure again rises. The analogy with two liquid layers has been actually found in solid solutions, in isomorphous mixtures as a matter of fact². Beryllium sulphate and selenate, e.g., do not mix isomorphically in all proportions, but between S:Se = 7.33:1 and S:Se = 4:1 there is a gap. So that from a solution containing, say, S:Se = 5:1 two isomorphous mixtures will crystallize out, one tetragonal (7.33:1), the other rhombic (4:1).

In following out further the behaviour of palladium hydride with regard to the molecular character of the hydrogen, only the parts of the series of observations before and after the region of constant pressure are available, and especially the former, because it refers to small concentrations of hydrogen, and so satisfies the condition implied in the theory of solution.

According to what precedes (p. 28), if the pressure and the concentration of hydrogen in palladium are proportional, the formula H_2 is probable for the dissolved gas. The following results are obtained, with the aid of the density of palladium hydride:—

<i>Pressure in mm. (p)</i>	<i>C.c. Pd, containing 2 mg. H (v)</i>	<i>pv</i>	<i>$v\sqrt{p}$</i>
26.2	3.084	80.8	15.8
82.8	1.827	151.3	16.6
165.4	1.299	214.8	16.6
393.7	0.771	303.5	15.3

¹ According to recent observations by v. Jüptner on steel, there are indications of a similar phenomenon involving solutions of carbon in iron.

² See also Part I, p. 55.

It appears that the concentration ($\frac{1}{v}$) is not proportional to the pressure, for $\frac{p}{c} = pv$ (where $v = \text{c.c. Pd, containing 2 mgr. H}$) varies from 80.8 to 303.5. On the other hand, $v\sqrt{p}$ is remarkably constant, as the fourth column shows. This means proportionality between the pressure and the square of the concentration, and from what precedes, makes it probable that the hydrogen is not at present dissolved as H_2 but as H , thus confirming the main conclusion that the solid state is not due to great molecular complexity.

II. MOLECULAR STRUCTURE

(*Isomerism, Tautomerism*)

WHILST so far we have been concerned with the size of the molecules, we have now to consider their internal structure. The necessity for going into this point lies in the existence of isomerism. From the moment that bodies of the same molecular magnitude and composition with different properties are known, such as ethyl- and dimethylamine, which, it is well known, both have the formula C_2H_7N , the possibility of different arrangements suggests itself as an explanation. For that reason the development of the theory of molecular structure has taken place in organic chemistry. Isomerism among inorganic compounds, such as between ammonium phosphite and hydroxylamine hypophosphite, both NH_6PO_3 , is rare¹.

In the methods now to be described for arriving at the molecular structure, the molecular formula, which gives the number and nature of the atoms in the molecule, serves as a starting-point. It may be obtained, as mentioned on p. 14, from the qualitative and quantitative composition and the molecular weight.

The further step towards molecular structure rendered necessary by isomerism is to find the mode of connexion of the atoms, a problem known as that of determining the structure or constitution. Then, the information derived

¹ Sabanejeff, *Berl. Ber.* 30. 285. See also the comprehensive investigations of Werner on metallic ammonium derivatives (*Zeitschr. f. anorg. Chem.*); also Kurnakow, *Berl. Ber.* 1898, p. 207.

in this way proving insufficient, conceptions going in further detail into the relative positions of the atoms were developed as a study of configuration or stereochemistry. We shall here discuss each in turn, and in a third section the very peculiar phenomenon known as tautomerism.

§ 1. DETERMINATION OF CONSTITUTION.

The study of constitution, then, refers to the mode of connexion between the atoms. In it the molecule is supposed motionless, so that the theory could at most only represent the facts accurately at the absolute zero.

Of the methods in question which allow of determining the mode of connexion, there are, of special importance:

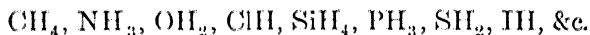
A. Determination of constitution on the basis of the valency of the elements combined.

B. Determination of constitution from formation out of, and conversion into compounds of known structure.

It may be added that many determinations of constitution are based on analogy, and therefore on the relations between physical and chemical properties and structure. But these will, according to the arrangement chosen, find their natural place in Part III.

A. Determination of Constitution on the Basis of the Valency of the Elements combined.

The notion of valency, on which this method is based, must first be quite briefly considered in its origin and extent. It is worth while then to glance at the binary hydrogen compounds of known molecular weight, in which only one atom of the other element occurs in the molecule, as:

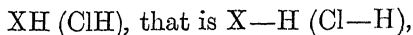


It appears then that never more than one atom of another element is combined with a single atom of hydrogen. This fact is expressed in the conception that hydrogen has only

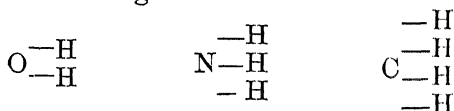
one faculty of combining, only one valency, as shown graphically by a stroke:



On the assumption that this faculty of combination is in the formation of the molecule used, and used up, mutually, it follows that all elements which combine with hydrogen according to the symbol

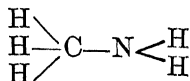


like chlorine, bromine, iodine, &c., have, like hydrogen, only one valency, or are univalent. They can, therefore, like hydrogen, be used to determine the valency. The elements that combine according to the schemes



are accordingly bi-, tri-, and quadrivalent.

Simple as the fundamental conception of valency appears, its further development is complicated because there are elements which do not always appear with the same valency, e. g. iron is bi- or trivalent according as it occurs in the so-called ferrous or ferric compounds. Valency would accordingly supply a very unreliable basis for determination of constitution were it not that in the department in which such determinations are important, namely, in organic chemistry, the elements mainly concerned do possess constant valencies. Hydrogen appears to be invariably univalent, oxygen almost always bivalent, carbon quadrivalent, so the somewhat empirical method practically followed on these grounds is of the highest importance, and usually leads directly to the object aimed at. Thus a compound with the molecular formula CH_5N can only, remembering the quadri-, tri-, and univalence of carbon, nitrogen, and hydrogen, have the constitution



valency: it may often be replaced or supported by methods to be described later, which then show their scientific superiority in the elucidation they give to the notion of valency.

B. Determination of Constitution from Formation out of, and Conversion into Compounds of known Structure.

In order to adhere to a definite example in this case too, we will discuss the constitution and isomerism of methyl mustard oil and methyl thiocyanate. The two compounds are known to have the same molecular formula, C_2H_3NS , and it was the relations of composition and decomposition that led Hofmann¹ to choose the appropriate constitutional formulae.

Formation of methyl mustard oil takes place, amongst other ways, from methylamine (CH_3NH_2) and carbon sulphochloride (Cl_2CS), with separation of hydrochloric acid:

$H_2CNH_2 + Cl_2CS = 2 HCl + C_2H_3NS$ (methyl mustard oil);
decomposition, e. g. under the influence of hydrogen (sodium amalgam and alcohol), to formation of methylamine and methylene sulphide (H_2CS):

C_2H_3NS (methyl mustard oil) + $2 H_2 = H_3CNH_3 + H_2CS$.

For the formation of methyl thiocyanate, on the other hand, we may use methyl sulphide (H_3CSCH_3) and bromocyanogen ($CNBr$). The thiocyanate is produced according to the equation

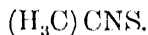
$H_3CSCH_3 + BrCN = H_3CBr + C_2H_3NS$ (methyl thiocyanate);

while decomposition by means of hydrogen leads to separation of methylmercaptan (H_3CSH) and hydrocyanic acid (HCN):

C_2H_3NS (methyl thiocyanate) + $H_2 = H_3CSH + HCN$.

¹ Beilstein, *Handbuch der organ. Chemie*, p. 699.

All these reactions lead to a common characteristic of the constitution of the isomers, viz. the presence of a methyl group (CH_3), which is regularly contained both in the materials required for formation and the products of decomposition. The constitution of each is therefore definite to the extent of being

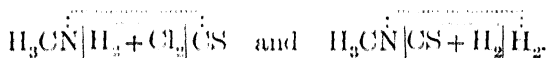


The difference is now simply shown in the above reactions, both by the materials required for formation and by the products of combustion, to lie in the fact that the methyl group of the mustard oil is connected to nitrogen; but that of the thiocyanate to sulphur. This may be expressed by the constitutional formulæ

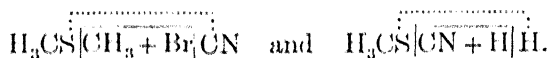
$\text{H}_3\text{CNC}\dot{\text{S}}$ (methyl mustard oil), $\text{H}_3\text{CS}\dot{\text{C}}\text{N}$ (methyl thiocyanate).

The following schemes will then serve to express the reactions:

For methyl mustard oil:



For methyl thiocyanate:

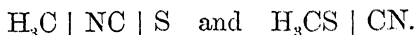


It should be noticed that in this choice, made on the ground that the formation and decomposition can easily be expressed, something has been assumed as to the course of the reactions, viz. that in reacting, a molecule changes as little as may be. To illustrate this by an example, we may note that hydrocyanic acid might conceivably be formed from a body $\text{H}_3\text{CNC}\dot{\text{S}}$ in this manner:



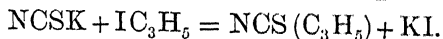
But then a double break would occur in the original

molecule H_3CNCS , whilst in formation from H_3CSCN only a single one, as shown by the symbols



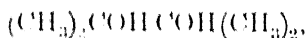
Intramolecular atomic displacements. The question thus becomes very important, whether this assumption as to the mechanism of reaction always corresponds to the facts. With regard to this, a distinction must first be made between inorganic and organic, i. e. carbon compounds. In the former, which show the phenomenon of isomerism exceptionally, or not at all, the product is independent of the original condition of the components; e.g. barium sulphate (BaSO_4) from oxide (BaO) and sulphur trioxide (SO_3) is identical with that from the superoxide (BaO_2) and sulphur dioxide (SO_2); here the peculiar rigidity which gives the compound the characteristic of its origin is absent. In organic compounds, however, with the appearance of isomerism, this is not the case. And that the rigidity is such that only the smallest possible change occurs in reactions, as in the case of mustard oil discussed above, is rendered probable by the fact that different determinations of constitution, all based on this principle, yield the same result: thus the formation and decomposition of methyl mustard oil lead to the same conclusion, and several other methods of formation and decomposition not mentioned here. There are cases, however, in which such agreement is wanting.

We may first consider such a case, which was at first difficult to understand, but was afterwards fully explained, so affording a prospect of removing other uncertainties previously existing. The body in question is allyl thiocyanate, $\text{NCS}(\text{C}_3\text{H}_5)$. The generally applicable method of preparation of thiocyanates, in which potassium thiocyanate (NCSK) is treated with the iodide of the radicle it is desired to introduce—in this case allyl (C_3H_5)—leads to a body of the required composition, according to the equation

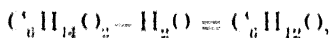


It however appears to be allyl mustard oil, $\text{SCN}(\text{C}_3\text{H}_5)$, instead of the thiocyanate, $\text{NCS}(\text{C}_3\text{H}_5)$. The explanation was given that this body is the result of a secondary reaction due to the somewhat high temperature (100°) employed. In the cold the allyl thiocyanate expected is actually formed, but it has the property of suffering an inversion on heating, i.e. being converted into the isomeric mustard oil. Two facts are thus simultaneously established: first, that an inversion of atoms within the molecule may stand in the way of determining constitutions by the method we are discussing; second, that to exclude such secondary changes, high temperatures should be avoided in determining constitution.

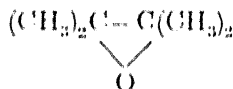
It has not so far always been found possible to analyse these modified reactions, and distinguish with certainty the primary reaction to be arrived at; e.g. pinacone, which has the constitutional formula



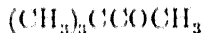
is converted by withdrawal of water into pinacolin



which accordingly was regarded by Friedel¹ as



But as Butlerow obtained the same body from trimethylacetyl chloride, $(\text{CH}_3)_3\text{COCl}$, and zinc methyl, $\text{Zn}(\text{CH}_3)_2$, the formula



was equally probable, according to the equation

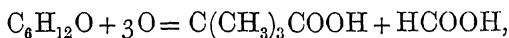


In one of the two reactions an extra methyl group must have been detached and displaced, and so far it is an open

¹ See among others Pomeranz, *Wien. Akad. Ber.* 106. 579 (1897).

question whether a subsequent process comes into play, or whether the displacement occurs during the reaction itself.

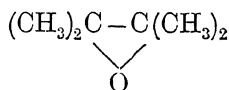
We may conclude hence, for the practice of determining constitutions, that a formula arrived at only in one way is uncertain, but that as such inversions are rare, when two processes yield the same result with regard to constitution, the uncertainty is small. The conclusion is strengthened when one process is one of formation, the other of decomposition, since then the possibility of the same subsequent change influencing the reaction is excluded. In this way the above case of pinacolin was decided; its decomposition on oxidation with formation of trimethylacetic acid, $C(CH_3)_3COOH$, together with formic acid,



has led to the adoption of the formula



The result would be still more conclusive if the existence of an isomer rendered impossible the choice of a second formula, i. e. in the case considered, if the body



were known and turned out to be different from pinacolin. Hence the case quoted on p. 86 of methyl mustard oil and methyl thiocyanate affords the greatest certainty, for formation and decomposition yield the same formula, and the other constitutional formula suits the mode of formation and decomposition of an isomeric compound.

§ 2. DETERMINATION OF CONFIGURATION.

(*Stereochemistry.*)

Whilst the study of constitution is restricted to determining the internal relations or bonds of the atoms in the molecule, the higher problem of finding the relative

positions of the atoms, i.e. the structure of the molecule, in the literal sense of the word, is included under configuration.

We will first describe the methods applied, and then devote a special section to stereochemistry, which developed through their application.

The two methods are essentially the following:—

A. Determination of configuration by the number of isomeric derivatives.

B. Determination of relative distances in the molecule.

The first method especially has led to valuable results; the second is at present chiefly of importance for its intrinsic scientific meaning.

A. Determination of Configuration by the Number of Isomeric Derivatives.

The wide applicability of the principle now to be discussed will be best appreciated by particular examples, of which cases may be chosen illustrating the fundamental meaning of the method. Such examples are those referring to the constitution of the benzene derivatives, and to stereochemistry.

1. *Constitution of Benzene*¹.

The molecular formula of benzene, C_6H_6 , allows of a large number of structural formulae in accordance with the indications of the theory of valency, and possessing an equal degree of probability. Several isomers, such as dipropargyl, are in this way possible.

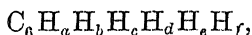
The choice was made by Kekulé on the ground of the number of isomeric derivatives, in particular because the monosubstituted bodies C_6H_5X , such as phenol, C_6H_5OH , exist in only one form, the disubstituted C_6H_4XY , such as oxybenzoic acid, $C_6H_4(OH)(COOH)$, in three isomeric forms.

¹ Marekwald, *Die Benzoltheorie*, 1897; Vaubel, *Der Benzolkern*, 1898.

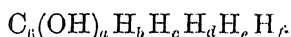
To decide more closely, we may add the fact that substituted benzenes are not capable of decomposition into pairs of active isomers¹.

Kekulé, in stating his view, relied empirically on the available experimental data. Ladenburg² gave later the strict proof, which will be repeated here.

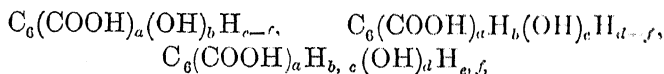
(a) *Benzene gives only a single monosubstituted derivative.* Let us distinguish the six hydrogen atoms in the following way :



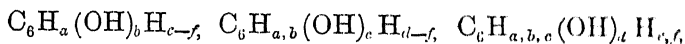
and regard phenol (C_6H_5OH) as



From phenol may be derived a benzoic acid, C_6H_5COOH , by replacing the hydroxyl group with chlorine (by means of PCl_5), the chlorine with methyl (by means of CH_3I and Na), the methyl with carboxyl (by oxidation); this benzoic acid therefore has the $COOH$ group in the a position. The three oxybenzoic acids, $C_6H_4OHCOOH$, derived from this acid, i. e. salicylic and meta- and para-oxybenzoic acids, differ on account of the OH group having replaced different atoms of hydrogen, and not that in a , therefore say those in b, c, d , yielding :



If now the calcium salts are distilled with lime, the carboxyl group is replaced by hydrogen, and we get the phenols :



which Ladenburg found to be identical with the original $C_6(OH)_aH_{b-f}$.

Thus substitution of the hydrogen atoms a to d in

¹ Van 't Hoff, *Atomlagerung im Raume* (2nd ed.), p. 92.

² *Theorie der aromatischen Verbindungen*, 1876.

benzene leads to the same product; this may be expressed symbolically as

$$H_a = H_b = H_c = H_d \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the second place it appears that in benzoic acid there are still two hydrogen atoms whose substitution leads to the same result.

Let us take e.g. the oxyacid, $C_6(COOH)_a(OH)_b H_{c-f}$, and convert the corresponding bromtoluene, $C_6(CH_3)_a Br_b H_{c-f}$, into nitrobromtoluene, $C_6(CH_3)_a Br_b(NO_2)_3 H_3$; this may be converted by reduction into an amidotoluene, $C_6(CH_3)_a H_b(NH_2)_3 H_3$, and the latter by diazotizing and treatment with bromine, into $C_6(CH_3)_a H_b Br H_3$, which is identical with the original substance. Accordingly in benzoic acid, $C_6(COOH)_a H_b$, one hydrogen atom is in a position identical with b , consequently either

$$H_b = H_c, \quad H_b = H_d, \quad H_b = H_e, \quad \text{or} \quad H_b = H_f.$$

The first two possibilities, however, disappear, since the corresponding oxyacids that have the OH in b , c , and d respectively are different, so there remain only the possibilities

$$H_b = H_a \quad \text{and} \quad H_b = H_f \quad . \quad . \quad . \quad . \quad (2)$$

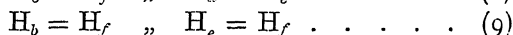
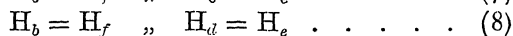
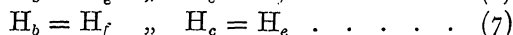
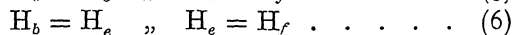
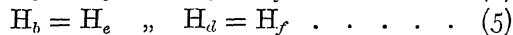
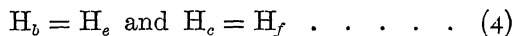
In the third place there is, besides H_b , still a pair of similar H atoms in benzoic acid, as appears from the fact that the oxybenzoic acid in question, $C_6(COOH)_a(OH)_b H_{c-f}$, gives a brombenzoic acid, $C_6(COOH)_a Br_b H_{c-f}$, which leads to two isomeric nitrobromobenzoic acids, $C_6(COOH)_a Br_b(NO_2)_2 H_2$, whose reduction gives the same amidobenzoic acid, $C_6(COOH)_a H_b(NO_2)_2 H_2$. Thus (as again $H_c = H_d$ is excluded on account of the difference between the corresponding oxybenzoic acids) either

$$H_c = H_e, \quad H_c = H_f, \quad H_d = H_e, \quad H_d = H_f, \quad \text{or} \quad H_e = H_f \quad (3)$$

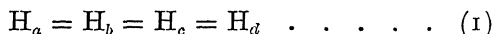
If (2) and (3) are combined, remembering that equivalence of b , c , and d is excluded, so that e.g. the combination

$$H_b = H_c \quad \text{and} \quad H_c = H_e$$

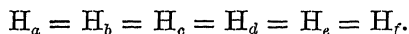
in benzoic acid is not allowable, the remaining possibilities are:



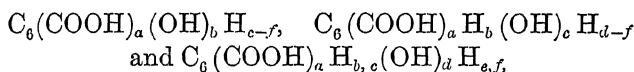
These hydrogen atoms must, then, have identical positions in benzene, and we have already



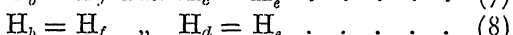
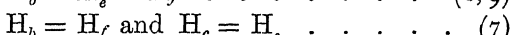
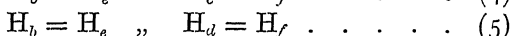
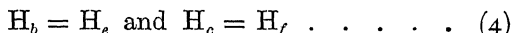
so that combination of (1) with the possibilities given by (4) to (9) leads to the conclusion



(b) The second fact, the existence of three disubstituted products, also assumed by Kekulé on the ground of the data then existing, is included in the foregoing as a necessary consequence. Besides the three oxybenzoic acids,



two other isomers are conceivable, with the hydroxyl group in the place of the hydrogen atoms H_e , H_f respectively. But we have seen that one of the six combinations (4) to (9) necessarily holds, and this makes the other two isomers impossible, since one of these equivalences must hold for benzoic acid, $C_6(COOH)_aH_{b-f}$, viz. :—



(c) The third fact, that the benzene substitution products, not containing asymmetrical substituting groups, cannot be separated into optically active isomers (proved at least for the trisubstituted compounds), shows that compounds of the

type $C_6(abcdef)$, i.e. with five hydrogen atoms replaced by different groups, $C_6HX_1X_2X_3X_4X_5$,

have a symmetrical constitution; for asymmetry implies a non-identical reflected image, so that we should expect two isomers differing—as we shall see later—by their opposite rotation of polarized light, their so-called optical activity.

This condition is only satisfied if benzene has a plane of symmetry, in which all the hydrogen atoms lie; in other words, all the hydrogen atoms are in one plane, with respect to which the carbon atoms are symmetrically placed. The suggested spatial arrangements of the hydrogen atoms are thus excluded. With Ladenburg's prism formula, e.g., even the diderivatives $C_6H_4X_2$ would suffer decomposition into optical antipodes, since the two symbols in Fig. 13 are not symmetrical, and therefore not identical reflected

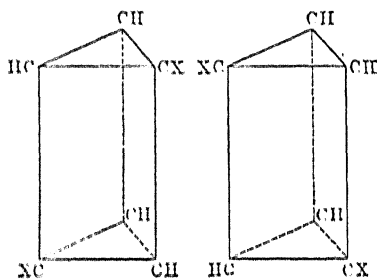
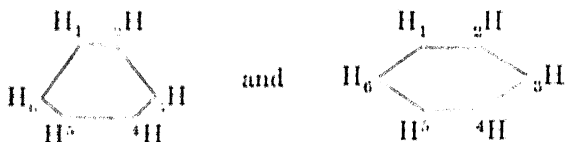


Fig. 13.

images; the assumption of the regular octahedron with the hydrogen atoms at the corner points carries one a little further, but there again the triderivatives would suffer decomposition.

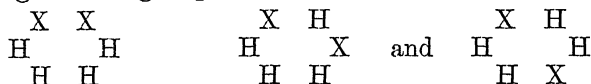
How the hydrogen atoms are arranged in the plane follows partly from the first principle, that there is only a single monoderivative, according to which the hydrogen atoms must be similarly situated. Two possibilities occur:



The second is the arrangement at the angles of a regular hexagon; the first at those of a hexagon with alternately

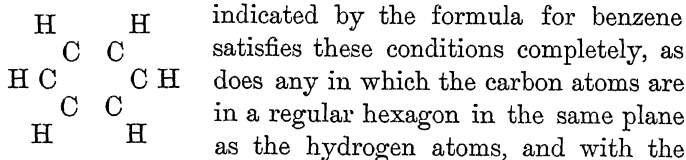
larger (2.3, 4.5, 6.1) and smaller (1.2, 3.4, 5.6) edges, very suggestive of Kekulé's formula with alternate single and double linkages.

The second principle, that three diderivatives, $C_6H_4X_2$, exist, settles the choice, since only the second possibility, the regular hexagon, provides the three isomers:

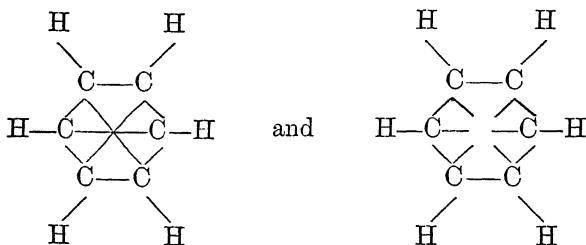


distinguished as 1.2 (ortho), 1.3 (meta), and 1.4 (para), whilst 1.5 = 1.3 and 1.6 = 1.2. With the irregular hexagon we should have four isomers, since 1.5 = 1.3, but 1.6 is not = 1.2.

The position of the carbon atoms is indeterminate, except that it must leave untouched the symmetry of the whole with respect to the plane in which the hydrogen atoms lie, and the identical position of the hydrogen atoms, whilst the number of diderivates remains three. An arrangement



same centre; either, therefore, the above, or the same figure rotated 30° . The symbol may, without losing its validity, be brought into accordance with the theory of valency in either of the following ways:—

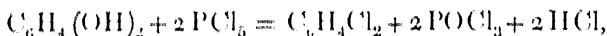


due respectively to Claus and to Armstrong and Baeyer (the so-called centric formula); in the latter it is assumed

that the fourth valencies of the carbon atoms do not saturate each other singly, but neutralize in their entirety.

2. Determination of Position in the Benzene Derivatives.

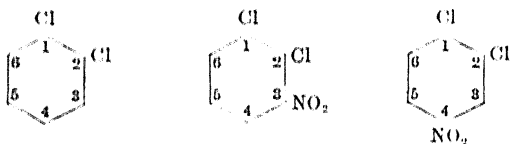
After the constitution of benzene was so far settled as to give an explanation of the existence of only one monoderivative, but of three isomeric diderivatives, the question arose, which of the three possible constitutions 1. 2 (ortho), 1. 3 (meta), 1. 4 (para) to attribute to any given diderivative. This is the problem known as absolute determination of position. Kekulé considered the answer as only partly possible, regarding experiment as limited to determining whether two compounds belong to the same series or not. E. g. which dichlorobenzene is to be grouped with any one of the three dioxybenzenes—say hydroquinone—can be found from the conversion of hydroquinone into dichlorobenzene by means of PCl_5 ,



taking care as far as possible to exclude an intramolecular displacement (p. 88). This is accordingly a relative determination of position.

The further problem of absolute determination is now to settle whether these two compounds, or rather the whole group they belong to, has the constitution 1. 2 or another.

Körner answered this question also by the method of the number of isomeric derivatives. He remarked that a diderivative, such as $\text{C}_6\text{H}_4\text{Cl}_2$ (1. 2), leads on introduction of a third group, say NO_2 , to two possible formulae, 1. 2. 3 and 1. 2. 4, as is shown by the diagrams:



whilst 1. 2. 5 = 1. 2. 4 and 1. 2. 6 = 1. 2. 3. But $\text{C}_6\text{H}_4\text{Cl}_2$

(1.3) gives three isomeric triderivatives, viz. 1.3.2, 1.3.4, and 1.3.5. Finally, $C_6H_4Cl_2$ (1.4) allows of only a single possibility, since $1.4.2 = 1.4.3 = 1.4.5 = 1.4.6$.

The application of these principles to a very complete collection of experimental material resulted in an unexceptionable solution of the problem, and one that accords satisfactorily with the indication of constitution given by the formation of benzene compounds out of, and their conversion into, fatty bodies.

B. Determination of Relative Distances in the Molecule.

The different atoms and groups in the same molecule may act on one another in a way that gives information as to their relative distances. This action may appear in two ways. First, it may lead to a reaction, caused by combination and partial separation of the two groups; but on the other hand the character of a group may suffer a change, which can often be followed out quantitatively.

1. *Mutual Action of Different Groups.*

An action that often occurs in the domain of organic chemistry is the combination of two hydroxyl groups with separation of water:

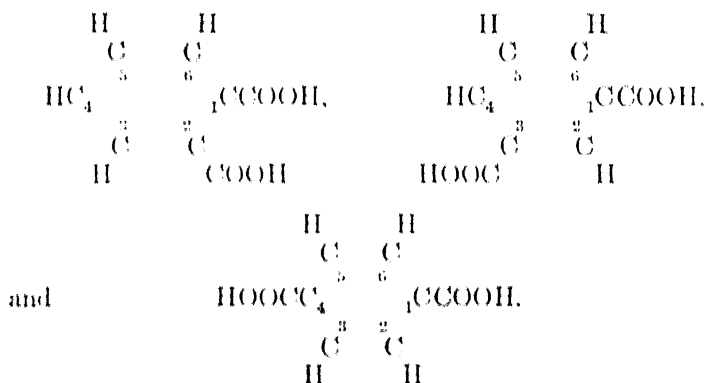


Of this an example may be quoted.

Many facts point to the part played by mutual distance in such actions, and especially, first, that in organic compounds, when two hydroxyl groups are attached to the same carbon atom, they at once suffer the change, or rather the existence of bodies containing the group $C(OH)_2$ is exceptional. Chloral hydrate, which appears to have the formula $CCl_3CH(OH)_2$, seems to be one of the few such compounds, whilst e.g. the attempt to form the corresponding compound, $CH_3CH(OH)_2$, leads to formation of aldehyde,

CH_3CHO , with separation of water. On the other hand, compounds containing the group $\text{C}(\text{OH})\text{C}(\text{OH})$, such as ethylene glycol, $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$, are mostly very stable. It must be remarked, however, and it adds to the difficulty of making rational use of the principle, that not only mutual distance, but other influences as well, affect the separation of water from two hydroxyl groups, as is clear from the case of chloral hydrate¹.

An interesting example from the aromatic compounds may be added, in which the method discussed led to a direct and reliable determination of constitution. The three phthalic acids, $\text{C}_6\text{H}_4(\text{COOH})_2$, have the configurations



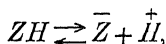
Now only one of them easily forms the anhydride, $\text{C}_6\text{H}_4(\text{CO})_2$, with separation of water; this one was therefore, and correctly, assumed to be orthophthalic acid (1.2), whilst the other formulae were assigned to isophthalic (1.3) and terephthalic acid (1.4): in the latter the carboxyl groups, COOH , containing the hydroxyl, are more widely separated.

It may be concluded in general that such condensation, i.e. formation of an internal anhydride with separation of water, occurs most easily in the orthoderivatives (1.2).

¹ See amongst others, measurements of velocity in the conversion of chlorhydrins. Evans, *Zeitschr. f. Phys. Chem.* 7. 356.

2. Mutual Influence of Different Groups.

The mutual action of two groups in a molecule may thus show itself in bringing about a combination, and chemical reaction between them; but without going so far as that it may suffice to change the character of one of the groups under the influence of the other. We may take as instance the acid character due to the group COOH ; this property may be strengthened or weakened, for the reason considered. Since Ostwald's dissociation constant offers a ready measure of the acid character, the principle of determination of constitution has been tested in this direction by the author¹ named. The dissociation constant K which governs equilibrium between undissociated acid and ions, according to the equation



and therefore bears the following relation to the concentration of the undissociated acid C_a and ions C_i (Part I, p. 118),

$$K = \frac{C_i^2}{C_a},$$

may easily be determined from the conductivity, since the dissociated part is the same fraction of the total concentration that the molecular conductivity μ for the concentration in question is of its limiting value μ_∞ , i. e.

$$C_i : (C_i + C_a = C) = \mu : \mu_\infty$$

Hence C_i and C_a are calculable for any given concentration, and therefore K is so:

$$K = \frac{C_i^2}{C_a} = \frac{C^2 \left(\frac{\mu}{\mu_\infty} \right)^2}{C \left(1 - \frac{\mu}{\mu_\infty} \right)} = \frac{C a^2}{1 - a},$$

whence a expresses the fraction dissociated into ions.

¹ *Zeitschr. f. Phys. Chem.* 3. 418.

The values of K thus measured are suitable for judging of the influence we are considering, not only on account of the facility of determination, but because they vary so greatly amongst themselves. Thus the influence of chlorine at 25° in strengthening an acid is shown by the numbers:

Acetic acid, CH_3COOH	100 $K =$	0.0018
Monochloroacetic acid, CH_2ClCOOH		0.152
Dichloroacetic acid, CHCl_2COOH		5.14
Trichloroacetic acid, CCl_3COOH		121

and in crotonic and isocrotonic acids, isomers of the formula $\text{CH}_3\text{CH}(\text{CHCOOH})$, chlorine shows, as might be expected, a greater influence on K when near than when far from the carboxyl; the numbers again refer to 25°:

	<i>Crotonic acid</i>	<i>Isocrotonic acid</i>
100 $K =$	0.00204	0.0036
α Chloro-derivative ($\text{CH}_3\text{CH}(\text{Cl})\text{COOH}$)	" = 0.072	0.158
β " " ($\text{CH}_3\text{C}(\text{Cl})\text{CHCOOH}$)	" = 0.0144	0.0095

Since we have here an indication of the possibility of determining relative distances within the molecule, we must mention the qualifications so far existing.

On the theoretical side it must be remembered that, in consequence of the unequal distribution of matter in the molecule, an action is rarely propagated equally in all directions within it.

On the experimental side it appears that sometimes a group in the meta-, sometimes one in the para-position behaves as if it were at the smaller distance. This is shown in the following ortho- (1.2), meta- (1.3), and para- (1.4) derivatives in the benzene series¹.

<i>Chloro-derivatives</i>		<i>Nitro-derivatives</i>			<i>Oxy-derivatives</i>
<i>Benzoic acid</i>		<i>Benzoic acid</i>	<i>Phenol</i>	<i>Aniline</i>	<i>Benzoic acid</i>
(1.2)	100 K 0.006	0.006	—	0.075	0.006
"	" 0.132	0.616	0.0183	0.0111	0.102
(1.3)	" = 0.0155	0.0345	0.0589	0.094	0.0087
(1.4)	" 0.0093	0.0396	0.0112	—	0.00286

¹ Loewenherz, *Zeitschr. f. Phys. Chem.* 25. 385.

The substituting group always exercises most influence in the ortho-position (1.2); benzoic acid is strengthened by chlorine and the nitro group to the greatest extent, and the latter too brings out the acid character of phenol and suppresses the basic character of aniline most in the ortho-position. But comparison of the meta- and para-derivatives leads to varying results, since chlorine exercises the greatest influence in the meta-, the nitro group in the para-position. The oxyderivatives appear to behave like those of chlorine, except that here the acid character is weakened in the para-position, while it is strengthened in the ortho- and meta-.

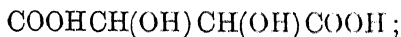
Velocity of reaction, which often in other ways goes with this dissociation constant, but is not usually so easy to measure, shows the same peculiarities, so the velocity constant k for some reactions¹ may be given here (see Part I, p. 191).

Combination of Brommethyl with Methylaniline (Toluidine) Chloraniline		Brommethyl with Methylaniline
(1.2) $k = 54$	9	13
(1.3) $k = 445$	23	86
(1.4) $k = 96$	34	52
(Aniline $k = 68$)		(Aniline $k = 24$)

The case is again simplest for the chlorderivatives: the velocity, 68 for aniline, is reduced, the most by chlorine in the ortho-position to 9, then in the meta- to 23, then in the para- to 34.

C. Stereochemistry.

Since constitutional formulae, expressing only the mode of combination of the atoms in the molecule, no longer sufficed to explain the cases of isomerism observed, a new attempt at explanation had to be made. Such a case arose in the discovery by Pasteur in 1853 of laevo-tartaric acid,



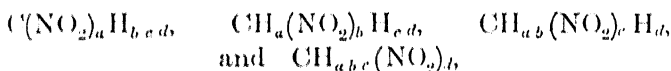
but in the then state of the study of constitution was not

¹ Menschutkin, *Berl. Ber.* 30. 2966, 31. 1423.

recognized as such. It was Wislicenus who first, in 1873, moved by the discovery of the isomeric active ethylidene-lactic acids, $\text{CH}_3\text{CHOHCOOH}$, expressed himself convinced that the usual constitutional formulae do not suffice to elucidate this isomerism.

Some extension of the theory of constitution was thus necessary, and of the three possibilities, dissimilarity in the valencies of carbon, displacement of the atoms, and the relative position of the atoms in space, the last, as is well known, turned out to be the satisfactory explanation¹.

Dissimilarity between the different valencies of the carbon atom is not suited to supply the explanation, because that assumption would require isomerism in even the simplest derivatives of the type $\text{C}(\text{X})_3\text{Y}$, such as chloromethane, CH_3Cl . It is of importance that Henry² carried out a systematic research on this point, preparing nitromethane, H_3CNO_2 , in four different ways, each of which would have brought the nitro group into the place of a different carbon atom. If, then, we distinguish the four hydrogen atoms by the indices $a b c d$, he prepared



which turned out to be identical.

The starting material for this was methyl iodide, CH_3I ; this, combined directly with AgNO_2 , was transformed into $\text{C}(\text{NO}_2)_a\text{H}_{bcd}$. Another portion was converted by KCN into the nitril of acetic acid, $\text{C}(\text{CN})_a\text{H}_{bcd}$, and then into acetic acid itself, $\text{C}(\text{COOH})_a\text{H}_{bcd}$; this was chlorinated to $\text{C}(\text{COOH})_a\text{Cl}_b\text{H}_{cd}$, and on treatment with AgNO_2 gave, through the transiently formed nitroacetic acid, $\text{C}(\text{COOH})_a(\text{NO}_2)_b\text{H}_{cd}$, the second nitromethane, $\text{CH}_a(\text{NO}_2)_b\text{H}_{cd}$. Another portion of the nitroacetic acid was then converted into malonic acid, chlorinated to $\text{C}(\text{COOH})_{ab}\text{Cl}_c\text{H}_d$, and reduced by AgNO_2 to the third nitromethane,

¹ Van't Hoff, *Lagerung der Atome im Raume* (2nd ed.), 1894.

² *Zeitschr. f. Phys. Chem.* 2. 553.

$\text{CH}_{a,b}(\text{NO}_2)_c\text{H}_d$. Renewed introduction of the carboxyl group, chlorination, and nitration yielded the fourth nitromethane, $\text{CH}_{a,b,c}(\text{NO}_2)_d$. The four nitromethanes thus arrived at were found, as already remarked, to be identical.

Further, we may briefly discuss the possible explanation of isomerism not falling within the theory of constitution, by differences in atomic movements. Berthelot¹ suggested it for the case of tartaric and lactic acids. The attempt, however, remained without success, as it was not possible to formulate the view clearly. It should be observed in this connexion that any attempt at explanation based on atomic movements requires that the phenomenon explained should vanish at the absolute zero, since there atomic and molecular movements cease. Fall of temperature should therefore lead to a gradual assimilation of the differences between isomers, if difference of atomic movement is the cause, and of this the isomers in question do not show the smallest indication.

The third alternative, *isomerism due to different positions of the atoms in space*, has² shown itself capable of meeting the case, and led to the development of stereochemistry. We will bring the subject forward in the following divisions:—

- (1) The asymmetric carbon atom and separation into optical antipodes.
- (2) Single carbon linkages, and compounds with more than one asymmetric carbon atom.
- (3) Double linkages and rings.
- (4) Stereochemistry of other elements.

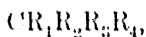
1. *The Asymmetric Carbon Atom and Separation into Optical Antipodes.*

Stereochemistry is based on the principle (p. 91) of determining configuration by the number of isomeric substitution products, supported and extended by application

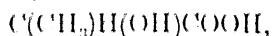
¹ *Bull. de la Soc. Chim.* 1875.

² *Walden, Journ. russ. Phys.-Chem. Ges.* 30. 483.

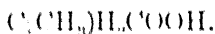
of the method (p. 98) depending on relative distances in the molecule. The fact is that in methane derivatives of the type



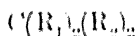
in which, therefore, the carbon is combined with four different atoms or groups, such as lactic acid, just mentioned,



two (oppositely optically active) isomers regularly occur. The difference of the groups or atoms is essential, since, e. g., if in the above the hydroxyl group be replaced by hydrogen, both isomeric lactic acids lead to the same (optically inactive) propionic acid,



A configuration of methane, such as is shown in Figs. 14 and 15, with the four groups R in one plane and uniformly arranged, would not agree with the facts, for then the type



with only two different groups should lead to isomerism, as shown by the difference between Figs. 14 and 15. But the

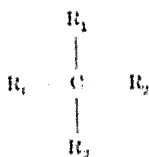


Fig. 14.



Fig. 15.

arrangement at the angles of a regular tetrahedron excludes isomerism in this and other cases, unless all four groups are



Fig. 16.

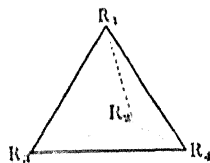
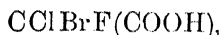


Fig. 17.

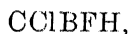
different, as is indicated by the difference between Figs. 16 and 17; this difference would obviously vanish if only R_3

and R_4 are alike. Not only the occurrence and non-occurrence of isomerism agree with this fundamental assumption, but also the character of the isomerism. In ordinary isomerism, as that of $C_6H_4Cl_2$ (1. 2) and (1. 3), there is a difference in every respect, in melting point, boiling point, solubility, density, and also in chemical behaviour. The two isomeric lactic acids, on the other hand, agree in almost all points, as in those just mentioned, in accordance with the complete equality of their internal dimensions. Differences occur only in respect to qualities that refer to the difference between two unsymmetrical reflected images, such as Figs. 16 and 17 are.

The most noticeable difference is in optical activity in the dissolved or the liquid condition; this shows itself in an opposite (and equal) rotation of polarized light, and every substance containing a carbon atom united to four different atoms or groups—a so-called asymmetric carbon atom—occurs in these two oppositely active forms, the optical antipodes. The simplest body yet known that illustrates this is chlorobromofluoroacetic acid¹,



which has been obtained in two antipodes, and from which, presumably, the isomeric chlorobromofluoromethanes,



should be got by splitting off carbon dioxide.

A second difference shown by the isomers in question is in their crystalline form. This expresses itself in the formation of two so-called enantiomorphic forms—due to hemihedry—such as Figs. 18 and 19 show for laevo- and dextro-ammonium bimalate. The two forms, like the diagrams

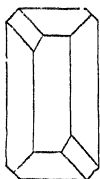


Fig. 18.

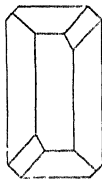


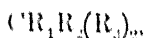
Fig. 19.

Figs. 16 and 17, representing the atomic arrangement, constitute a pair of unsymmetrical

¹ Swartz, *Bull. de l'Acad. de Belg.* (3) 31. 28.

reflected images, that cannot be superposed on one another.

The similarity of the antipodes in other respects implies the necessity of a separation, when a body with an asymmetric carbon atom is prepared in the laboratory. For starting with an inactive, symmetrical body, such as



when a fourth different group R_4 is introduced in place of one R_3 , the two R_3 groups, being symmetrically contained in the molecule, are replaced with equal facility, and so an inactive mixture of the two isomers, $C(R_1R_2R_3R_4)$, in equal amounts is produced, in which the components are yet to be separated. It is well known that in the organism, on the other hand, the antipodes occur separately, e.g. tartaric acid obtained from grapes is the active dextro-rotary modification.

The methods of separation available may be grouped as follows:—

- (a) Methods based on the phenomena of solution.
 - (a) So-called spontaneous separation.
 - (β) Separation by means of active compounds.
- (b) Methods based on chemical behaviour, depending on the action of enzymes and organisms.

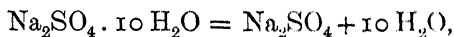
(a) Methods based on the Phenomena of Solution.

(a) Spontaneous separation. Separation of the optical antipodes is rendered difficult by their similarity of behaviour in almost every respect, especially their equal solubility; moreover, the isomers mostly unite to form a so-called racemic body, as in the classical example of the racemic acid precipitated on mixing concentrated solutions of the two oppositely active tartaric acids.

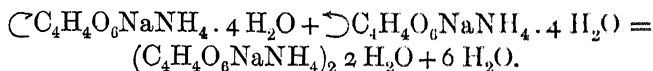
The fact discovered by Pasteur, that the substances do not always appear together in this way, but that, e.g., from the solution of the sodium-ammonium salt of racemic acid laevo- and dextro-sodium-ammonium tartrates crystallize

side by side, led to the first actual separation. This fact has since acquired a certain general interest in natural philosophy. Pasteur, who held the view that optically active compounds could only be obtained by the action of living organisms, attributed the so-called spontaneous separation to the action of germs in the atmosphere. Wyruboff opposed this view, and since then the mechanical explanation of the separation has become clear, viz. that separation takes place regularly when the mixture of the optical antipodes is less soluble than the racemic substance. The phenomenon depends on temperature, and for some bodies occurs only under restricted conditions of temperature, as will be seen from the following more detailed account of particular cases.

Städel found that the solution, which in Pasteur's hands yielded the two sodium-ammonium tartrates, gave him only a sodium-ammonium racemate; this was more thoroughly investigated by Scacchi, whilst Wyruboff found that the appearance of one or the other from solution depended on temperature; that if supersaturation was avoided the mixed tartrates appeared below 28°, the racemate above. Van't Hoff and van Deventer¹ then showed that we have here to do with a transition (Part I, p. 25). Just as with Glauber salt, the separation of hydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) or anhydride, according as one works below or above 33°, is associated with the complete transition of the salt at 33°, according to the equation



so the alternative crystallization of mixed tartrates or of racemate is associated with a transition taking place at 28°, according to the equation



The two phenomena may be observed in the same manner.

¹ *Zeitschr. f. Phys. Chem.* 1. 173; van't Hoff, Goldschmidt, Jorissen, l. c. 17. 49.

The transition of Glauber salt appears as a melting point, and can be determined either as the temperature at which that salt melts, or that at which a mixture of anhydrous sodium sulphate and water freezes. Beckmann's apparatus for exact determination of melting points is admirably adapted to the observation.

The same can be done for the formation and decomposition of racemates, and in that way, e. g., the temperature (40°) at which rubidium racemate splits up into the optical antipodes has been determined¹.

Since, however, a somewhat large amount of material is needed to determine transition temperatures in this way, the dilatometric process described in Part I, p. 25, in which the change of volume accompanying transition is used as indication, is often to be preferred. A dilatometer filled with the tartrate mixture, e. g., gave, as indication of the transition of the sodium ammonium tartrates into racemate, the following readings of the level of the liquid:

16.7	350 mm.	{	16 per 1°		
26.7	310 "		{	162 " 1°	
27.7	272 "			{	14 " 1°
30.7	227 "				

The conversion, therefore, took place between 26.7° and 27.7°, with an expansion equivalent to a rise of the liquid by $162 - 14 = 147$ mm.

As in the case of Glauber salt, so in that of the racemate, the transition is connected with a singularity in the solubility curve. This for Glauber salt shows a break at 33°, due to the intersection at that temperature of two solubility curves, one referring to the hydrate, the other to the anhydride (Part I, p. 66). The following numbers, taken from Lowel, will serve to illustrate this; they give the weight of anhydrous sodium sulphate per 100 parts of water in the saturated solution:

Saturated sol.	31.44°	32.05°	34°
Na ₂ SO ₄ . 10 H ₂ O	40	49.78	55
Na ₂ SO ₄	49.91	49.78	49.50

¹ Van 't Hoff, Müller, *Ber. Ber.* 31, 2206.

The numbers show that below 32.65° the solution saturated for anhydride is supersaturated with respect to $\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$; here we are clearly dealing with the well-known supersaturated Glauber salt solution. Above 32.65° the state of affairs is reversed, and the solution saturated for the hydrate is the more concentrated. The two facts accord with the reversible transition in one or the other direction.

The tartrate mixture and racemate show precisely similar behaviour. For 100 molecules of H_2O there were found, expressed in molecules of $\text{C}_4\text{H}_4\text{O}_6\text{NaNH}_4$:

For Saturation with	16.7°	27°
Tartrate mixture	2.43	3.86
Racemate	3.19	3.86

Only the solubility curve could not be followed out higher,

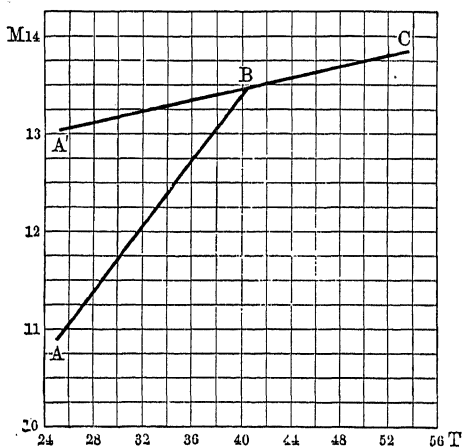
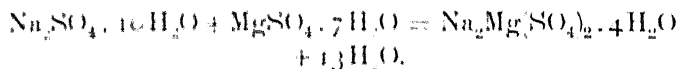


Fig. 20.

because a second transition into sodium and ammonium racemates takes place. For this reason rubidium racemate is better suited to show the point, having a corresponding transition at 40° . Measurements of solubility gave, expressed in molecules of $\text{C}_4\text{H}_4\text{O}_6\text{Rb}_2$ for 100 molecules of water:

Saturation with	25°	35°	40·4°	40·7°	54°
Tartrate mixture . . .	13·03	—	—	13·46	13·83 (Line A'B Fig. 20.)
Racemate	10·91	12·63	13·48	—	— (Line AB „ „)

Whilst, therefore, comparison with a simple transition between two hydrates (as of Glauber salt) brings out evident relationships, there is a difference to be noted, for the formation or decomposition of a racemate is not a simple conversion of one salt into another, but of a salt mixture (tartrates) into a single salt (racemate) or vice versa. Remembering this, it is clearly the formation or decomposition of double salts that should be quoted as analogy, and we will therefore describe what is essential in the relations of solubility at the transition temperature in such cases. (See Part I, p. 81.) Let us take the formation of astrakanite, the sodium-magnesium sulphate, $\text{Na}_2\text{Mg}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, from its components, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, which takes place at 22° according to the equation



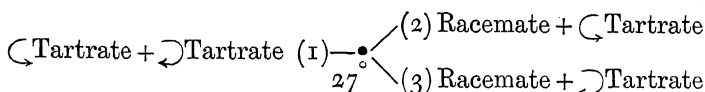
Here, again, we have an apparent fusion that may be followed by the thermometer or dilatometer.

We now find, in the behaviour with regard to solution, new relations to the formation of a racemate. These appear in the fact that at 22° three solubility curves intersect. From low temperatures up, we have the solution saturated for the two sulphates (1); at 22° formation of astrakanite sets in, and according as there is excess of the sodium or magnesium salt, we reach either the curve of saturation for astrakanite and sodium sulphate (2), or that of astrakanite and magnesium sulphate. Schematically:



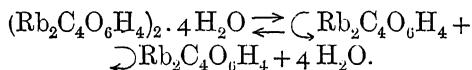
The same is to be expected for the formation of racemate. Thus, for the sodium-ammonium salt from low temperature

to 27° the saturation curve for the tartrate mixture (1) holds; at 27° formation of racemate occurs, and if the two tartrates are present in equal amounts, we obtain the former racemate curve. If one or other tartrate is present in excess, we come in the one case to the curve of saturation for racemate and dextro-tartrate (2), in the other to that for racemate and laevo-tartrate. Schematically:



The results of such measurements of solubility may best be represented by a model, in which the quantities of the two salts are measured along two perpendicular planes, whose line of intersection constitutes the axis of temperature. The solubility curves then lie between the two planes, and any projection of them can be obtained, such as Fig. 21.

The essential difference between the formation of a double salt and a racemate now appears in the symmetry possessed by the latter case, due to the exactly equal solubilities of the optical antipodes, whereas the components of a double salt have in general different solubilities. The number of measurements needed to prepare the model is for this reason smaller in the case of the racemate, and it is only necessary to experiment with the racemate, or inactive mixture, and one of the antipodes. This is the case with rubidium racemate: only here the phenomenon is reversed as compared with double-salt formation, for the formation of racemate takes place at lower temperatures, and in the equation



the left-hand side represents the form stable at low temperatures (below 40.4°). Thus, what in the preceding equation came on the left, the tartrate mixture (1), comes

here on the right, and conversely the mixture of racemate with the respective tartrates (2) and (3) comes here on the left.

Solubility measurements of the racemate-tartrate mixture gave per 100 molecules of water, expressed in molecules of $\text{Rb}_2\text{C}_4\text{O}_6\text{H}_4$:

Temperature	r-Tartrate	l-Tartrate	$\frac{r-l}{r+l}$
25°	9.15	2.8	0.531
30°	8.46	4.11	0.346
35°	7.8	5.12	0.208
40.4°	6.74	6.74	0

Fig. 21 is the projection of a model that represents these data. T is the axis of temperature; dextro-tartrate is

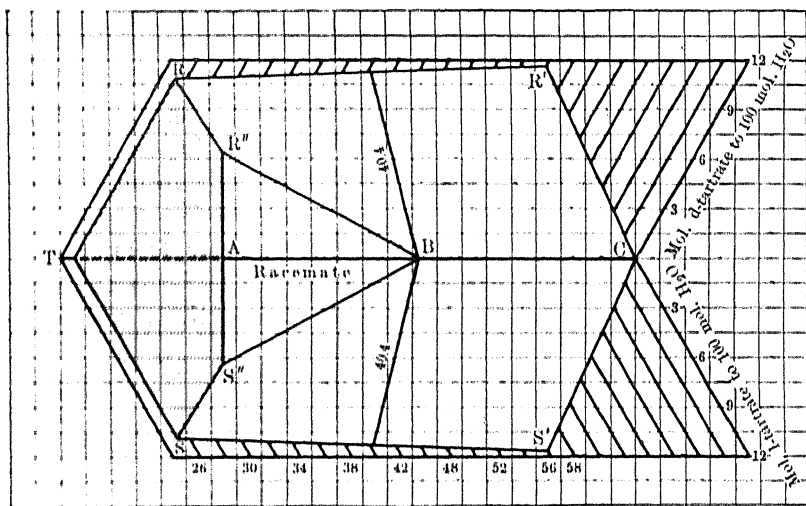


Fig. 21.

measured upwards, laevo-tartrate downwards, so that R''B represents the data just given, while AB and BC correspond to those that are also drawn on Fig. 20, and refer respec-

¹ The way in which the relative excess of one antipode approaches zero is very characteristic of the transition temperature.

tively to racemate without excess of either active tartrate, and to the tartrate mixture. To complete the figure in the plane of the dextro-tartrate, the line RR' is drawn for the solubility of the dextro-tartrate alone, from the data

25°	100 H ₂ O	10.0 Rb ₂ C ₄ O ₆ H ₄
52.5°	„	11.79 „

We may now, on account of the solubility of the two antipodes, draw on the same figure $s''B$ and ss' as expressing saturation with racemate and laevo-tartrate, or with the latter alone, and joining these various lines by surfaces we have

area $RR'CBR''$	saturation for dextro-tartrate ;
„ $ss'CBS''$	„ „ laevo-tartrate ;
„ $R''BS''$	„ „ racemate.

The bounding lines refer to saturation for two salts; the point B , in which they meet, to saturation for all three.

According to what precedes, inactive bodies containing asymmetric carbon may be divided into three classes :

1. Those, the most, that appear in racemic form, like racemic acid, and whose transition point is so far removed from ordinary temperatures that they appear from the inactive solution practically only as racemoids; the racemoid here has a much smaller solubility than the inactive mixture.

2. Others, rarer, that appear split up, like gulonic lactone; here the racemoid has a much greater solubility than the inactive mixture.

3. The third category includes the rarest cases, so far observed only in sodium-ammonium racemate, ammonium-bimalate, rubidium, and potassium racemates and methyl-mannosid, in which, according to the temperature, cases 1 and 2 meet, so that a transition point separates the regions of the two phenomena.

(β) *Separation by forming salts with active acids and bases.* A method very suitable for separation, when dealing with bases or acids, is to combine with suitable active

substances to form salts. The method was first applied in the case of racemic acid by Pasteur, who saturated the acid with cinchonine and found that the cinchonine salt of the laevo-acid crystallized first; this has then obviously a smaller, and therefore a different solubility¹, in accordance with the general rule that, so soon as asymmetrical optical antipodes combine with the same asymmetrical active substance, a compound results no longer answering to a pair of reflected images, as appears from Fig. 22.

The two larger triangles represent dextro- and laeo-tartaric acid, the two smaller, cinchonine; the dextro and laevo combinations cannot be arranged symmetrically to one another, and consequently differ in their properties like ordinary isomers, e. g. in their solubility. Direct measurements of solubility have not yet been carried out for such a case, so that the question is still undecided whether racemism is possible in it, with a transition temperature in the former sense². If so, the phenomena would be strictly comparable with the behaviour of double salts.

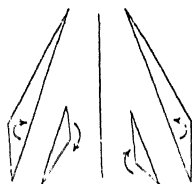


Fig. 22.

(b) *Methods of Separation depending on Chemical Action.*

Separation by means of enzymes and organisms. Separation by means of enzymes and organisms is really the same, for the function of an organism in such cases can be traced to the action of peculiar substances formed in the organism, and given off by it, to which the name of enzymes has been given. An especially interesting example of this is to be found in the isolation effected by Buchner³ of the enzyme of fermentation, zymase, from yeast, by breaking up the yeast-cells (by rubbing with glass) and pressing out. If we combine this fact with the discovery of Fischer⁴, that

¹ Marckwald, *Berl. Ber.* 31. 786.

² Ladenburg, *l. c.* 31. 524, 937, 1969; Küster, *l. c.* 31. 1847.

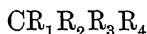
³ *l. c.* 31. 568, 1084, 1090.

⁴ *l. c.* 23. 2620.

only ordinary glucose, i. e. *d*-glucose, is capable of fermentation, but not its antipode, *l*-glucose, so that the latter may be prepared from the inactive *i*-glucose by fermentation, we have a good picture of what is so far known with regard to this subject. The mode of action of the enzyme is still completely unknown; it may be mentioned, however, that in some cases (conversion of maltose into glucose¹) the process is reversible, the possibility resting on fine details of constitution².

2. *Single Carbon Linkages and Compounds with more than one Asymmetric Carbon Atom.*

The principle of free rotation. Whilst so far we have dealt practically only with simple asymmetry, in compounds of the type



we have now to turn to single linkages between several carbon atoms and the appearance of multiple asymmetry.

It is a consequence of the fundamental conception of stereochemistry that in such single linkage one carbon atom lies at one of the angles of the tetrahedron, at whose other angles are the three groups combined with the other carbon atom; this is shown in Fig. 23. The line joining the two carbon atoms is thus fixed, leaving the three attached groups capable of rotation about it. Different positions of these groups causes an isomerism that has so far only been observed in rare cases, and perhaps not certainly there³. Thus

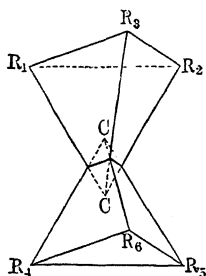


Fig. 23.

the mutual action of the groups attached to the carbon atoms seems in general to determine a single (preferential) relative position, corresponding to the only known, actually

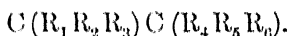
¹ Hill, *Journ. Chem. Soc. Trans.* 1898, 634.

² Fischer, *Bedeutung der Stereochemie für die Physiologie; Zeitschr. f. Phys. Chem.* 1898, p. 60.

³ Aberson, *Die Apfelsäure der Crassulaceen; Berl. Ber.* 31. 1432.

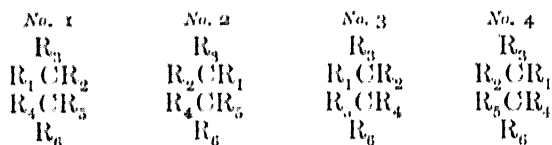
prepared compound. This position may be chosen so that the six groups combined with the two carbon atoms lie opposite one another in pairs, as in Fig. 23.

Number of isomers in multiple asymmetry. From the standpoint thus adopted the number of isomers is only increased by single linkage with a second carbon atom when a new asymmetric grouping is so introduced, as e. g. in a compound of the general type



The number of isomers in this case is two on account of the one carbon atom, and is doubled by the presence of the other, consequently four. In the same way, if n such carbon atoms unite the number becomes 2^n .

The arrangement and behaviour of these isomers may, in the case of two asymmetric carbon atoms, be made clear by the use of Kekulé's wire model, and may be represented on a plane by appropriate projection. Taking for that purpose Fig. 23 as starting-point, R_1, R_2, R_4 , and R_6 lie on the plane of the diagram; then R_3 may be brought into it by rotation upwards, about an axis passing through R_1, R_2 , and R_6 by rotation downwards about an axis passing through R_4, R_5 . We thus get the substance represented by the formula No. 1 following, and the three isomers are Nos. 2, 3, and 4:



It appears from this mode of representation that the four isomers are arranged in pairs 2 and 3, 1 and 4, each group including two configurations behaving as opposite reflected images, and are thus the expression of optical antipodes like those that occur with a single asymmetric carbon atom. This behaviour is still more easily understood by considering the optical rotation due to each carbon atom

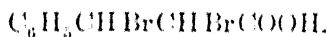
separately, which we may write A and B , $-A$ and $-B$. The rotations then are :

$$\begin{array}{cccc} \text{No. 1} & \text{No. 2} & \text{No. 3} & \text{No. 4} \\ A + B & -A + B & A - B = -(-A + B) & -A - B \\ & & & = -(A + B). \end{array}$$

These possibilities are easily realized by combining an acid and base, each of which occurs in two opposite active modifications, such as lactic acid and coniine. The four possible salts then are :

$$\begin{array}{cccc} \text{No. 1} & \text{No. 2} & \text{No. 3} & \text{No. 4} \\ A + B & -A + B & A - B & -A - B. \\ d\text{-lactic acid, } d\text{-coniine} & l\text{-lactic acid, } d\text{-coniine} & d\text{-lactic acid, } l\text{-coniine} & l\text{-lactic acid, } l\text{-coniine} \end{array}$$

As an example of this fourfold isomerism in a single body the dibromocinnamic acids may be chosen :

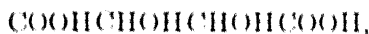


The two asymmetric carbon atoms are distinguished by underlining. It is well known that Liebermann succeeded in obtaining from cinnamic acid, $\text{C}_6\text{H}_5\text{CH}(\text{H})\text{COOH}$, by addition of bromine, an inactive mixture or racemic compound which could be split up into the pair of the one type. The other pair was obtained in a similar way from allo-cinnamic acid, which is isomeric with cinnamic acid.

Inactive undecomposable type. A separate discussion is required for the case, which may be regarded as a special case of the above, in which the atoms or groups attached to the two carbon atoms are similar in pairs, i.e.

$$\text{R}_1 = \text{R}_4, \quad \text{R}_2 = \text{R}_5, \quad \text{R}_3 = \text{R}_6,$$

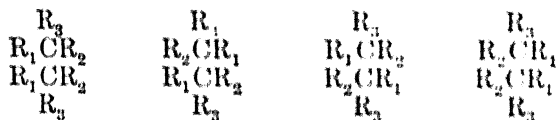
as in tartaric acid,



in which

$$\text{R}_1 = \text{R}_4 = \text{H}, \quad \text{R}_2 = \text{R}_5 = \text{OH}, \quad \text{R}_3 = \text{R}_6 = \text{COOH}.$$

The four former symbols then become :



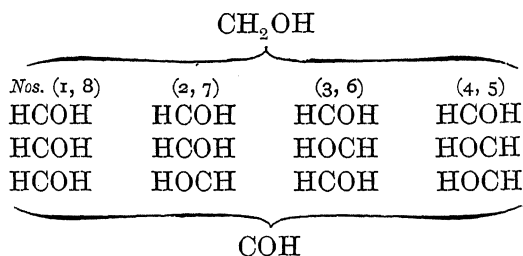
There arise therefore four types, each including a pair of antipodes :

1, 8 2, 7 3, 6 4, 5.

As an example we may take the pentoses



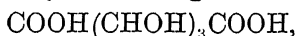
and considering only the types, we have



Actually these four types are found, in arabinose, ribose, xylose, and lyxose, of which arabinose is known in the two oppositely active forms, while of the other three types one antipode of each is wanting.

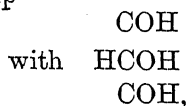
A definite choice of one of the four formulae, say for arabinose, may now be made on the following two grounds :—

1. Arabinose is oxydized to a glutaric acid,



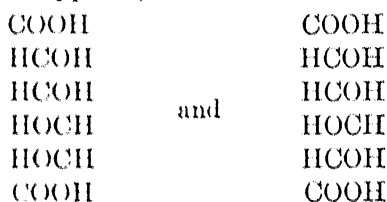
which is active. In this way the possibilities Nos. (1, 8), and Nos. (3, 6) are excluded, since they would lead to a glutaric acid with symmetrical configuration, and therefore of the inactive undecomposable type.

2. Glucose and mannose are formed from arabinose by replacing the group

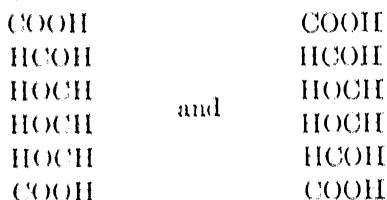


two isomers of the formula $\text{CH}_2\text{OH}(\text{CHOH})_4\text{COH}$ being produced; first, according to Kiliani and Fischer, hydrocyanic acid is added, the nitril produced converted into

acid, and the acid into aldehyde. These two isomers, glucose and mannose, are converted by oxydation into saccharic and mannosaccharic acids, with the formula $\text{COOH}(\text{CHOH})_4\text{COOH}$, which are active, a fact only compatible with type 2, 7 which leads to the bodies

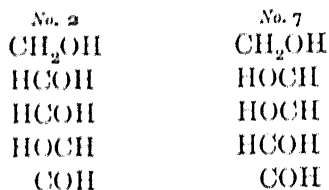


whilst type 4, 5 would lead to these:



of which the latter is symmetrical, and belongs to the class of inactive undecomposable modifications.

Whilst therefore the configuration may, reasoning from the necessary symmetry of the inactive undecomposable type, be traced out into detail, it remains undecided which of the two enantiomorphic forms 2 and 7 is to be identified with a given arabinose.



3. Double Linkage and Ring Formation.

Carbon double linkage may be represented graphically by a pair of tetrahedra, as in Fig. 24, which are so connected as to use up two bonds on each side. The other four then

lie in a plane, and the configuration of a compound, $C(ab)C(cd)$, is expressible by the formula



which shows at the same time that there are two possibilities, and that whether the two atoms or groups ab combined with carbon are the same as or different from cd . It is well known that in this case also isomerism is found, and we may discuss this more fully by considering fumaric and maleic acid. These two acids are expressible by the formulae

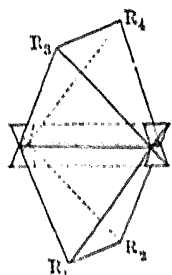
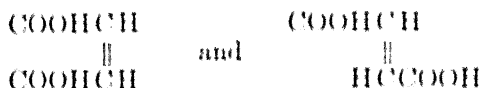
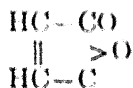


Fig. 24.



and correspond in their behaviour to what might be expected from the difference between these configurations.

In the first place, we are dealing with an isomerism of quite a different kind to that due to a single asymmetric carbon atom. The formulae are symmetrical, and so there is no optical activity and enantiomerism of crystalline form to be expected; but, on the other hand, we must not expect the exact agreement in properties—specific gravity, melting point, &c.—which is produced by the agreement in internal structure when isomerism is due to an asymmetric carbon atom. If we follow out the differences further, we find them in very good accord with the conception of their internal structure arrived at. In the first place, one of the acids, maleic, gives an anhydride very easily:

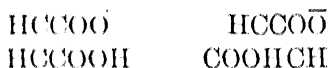


which is in accordance with the proximity of the two carboxyl groups in the formula. In the second place, this

same acid is the stronger, as might be expected from the influence exerted by the oxygen of either carboxyl on the other carboxyl group, which is close to it. The dissociation constants, which are closely related to the strength of an acid (Part I, p. 137), are respectively ¹

$$K_{\text{Mal.}} = 1.17, \quad K_{\text{Fum.}} = 0.093.$$

Thirdly, the acid salt of maleic acid is weaker than that of fumaric ², just because in the ions of these salts,



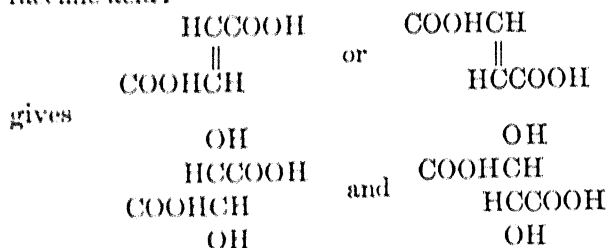
the negative charge opposes further dissociation, and does so more strongly in maleic acid, as being nearer. The quantity dissociated, found by means of the rate of inversion, is

<i>r</i>	<i>Diss. Maleic Acid</i>	<i>Diss. Fumaric Acid</i>
64	0.342 %	0.932 %
128	0.55 "	1.52 "
256	0.918 "	2.74 "

Finally the above formulae are confirmed by the results of oxydation in aqueous solution. Permanganate gives with maleic acid, on taking up hydroxyl, inactive undecomposable tartaric acid, as is to be expected :



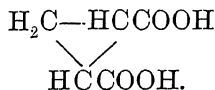
whilst fumaric acid gives, under the same circumstances, racemic acid :



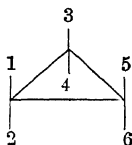
¹ *Zeitschr. f. Phys. Chem.* 3. 380.

² *l. c.* 25. 241.

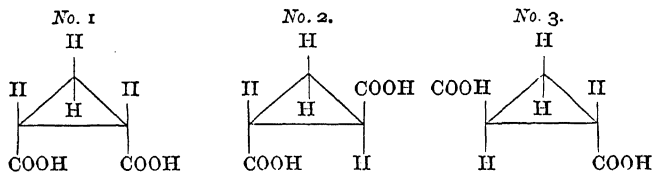
Ring formation. Finally we may consider the leading conclusion of stereochemistry as applied to the formation of rings, and in particular to the case of trimethylene dicarboxylic acid,



Representing such a ring in the following way:



with the six attached groups at 1 to 6, there are these possibilities:



Formula 1 represents a symmetrical, and therefore inactive form; Nos. 2 and 3 a pair of asymmetrical images, consequently active. Actually two inactive isomers are known, of which perhaps one is the unseparated mixture or racemic compound of Nos. 2 and 3.

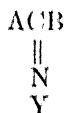
4. Stereochemistry of other Elements.

The spatial considerations applied with so much success to the carbon compounds may be extended to compounds of other elements. We will here only mention what refers to nitrogenous bodies.

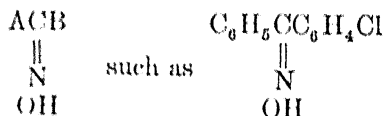
First must be considered the possibility of separation into optical antipodes, suggested by Le Bel in the case of isobutylpropylethylmethyllummonium chloride: unfortunately the researches on this point are only fragmentary,

and it is at present uncertain if the observed activity is to be ascribed to an active ammonium chloride.

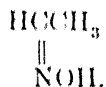
On the other hand, isomerism in bodies of the type



is fully established, both in the acetoximes which are derived from an asymmetrical ketone, i. e.



and in the aldoximes which correspond to the special case $\text{B} = \text{H}$, a simple example being acetaldoxime :



The two isomers thus arising are inactive, but differ physically like ordinary isomers, and chemically, amongst other ways in that one compound easily gives off water with formation of a nitril, which may be supposed due to proximity of the hydroxyl to hydrogen. The structural difference is therefore to be expressed by the formulae



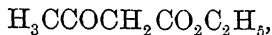
which recall those of fumaric and maleic acid.

Concluding remark on stereochemistry. As in determining constitutions in the earlier cases intramolecular displacement of the atoms may lead to wrong conclusions, making it desirable for a satisfactory determination to have two lines of argument, so in the more exact determination of configuration in stereochemistry the same thing must be borne in mind. Such direct changes have indeed often been observed within the region of stereo-

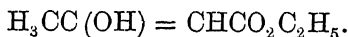
chemistry, e.g. the active bromosuccinic esters gradually lose their power of rotation, by becoming converted into a mixture or compound of the optical antipodes¹. This phenomenon is one especially noticed in halogen, and chiefly in bromine compounds, and probably explains why reactions carried out on such compounds have often given quite unexpected results; one of the most remarkable instances is that active bromosuccinic acid gives one malic acid with alkalis, but with silver oxide the optical antipode². At present, therefore, these halogen compounds should, as far as possible, be excluded from determinations of constitution in this province.

§ 3. TAUTOMERISM.

The phenomenon of tautomerism is that a compound shows an apparently different constitution according to the reagent that acts on it. This has been observed, e.g., in aceto-acetic ether, $\text{C}_2\text{H}_5\text{OCH}_2\text{CO}_2\text{C}_2\text{H}_5$, and led to two constitutional formulae, one proposed by Frankland,



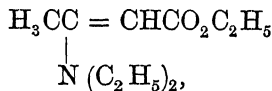
and the other supported by Geuther,



The first formula is based, *inter alia*, on the fact that with potash a decomposition takes place with formation of acetone,



The second is in accord with the formation *inter alia* of the body:



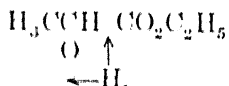
by the action of diethylamine, $\text{HN}(\text{C}_2\text{H}_5)_2$.

The explanation of this peculiar behaviour was sought

¹ Walden, *Berl. Ber.* 31. 1416.

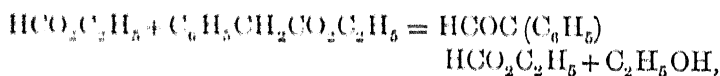
² l. c.

for by Laar¹ in a movement of the hydrogen atom, indicated in the following symbol:

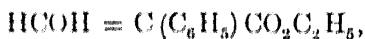


It has of late been suggested² that tautomerism corresponds to a mixture of two isomers in chemical equilibrium. Fundamentally these two conceptions agree, only the first is the molecular-mechanical view of the fact formulated in the latter. We will therefore recount the facts on which the latter formulation is based.

In the first place the supposed isomerism has been observed in certain cases in closely allied bodies. Wilhelm Wislicenus³ observed this, e.g., in formylphenylacetic ether, which is very similar to aceto-acetic ether. Obtained from ethyl formate and phenyl-acetate:



the body in question behaves as if containing hydroxyl:



e.g. it gives an addition product with phenyl-cyanate, OCNC_6H_5 . On melting (indefinitely between 60° and 70°) an alteration sets in; solidification does not take place, and the substance, now liquid at ordinary temperatures, retains indeed the same molecular weight, but colours with ferric chloride, and behaves like an aldehyde. This modification is known as the 'aldo-form' (the former as 'enol-'), and is represented by the formula



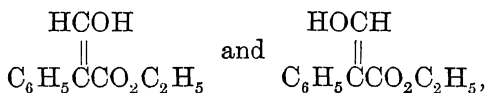
The reconversion is accomplished by potassium carbonate, in which the solid compound at once dissolves, but the

¹ *Berl. Ber.* 18, 648, 19, 730.

² S. Traube, *l. c.* 29, 1715.

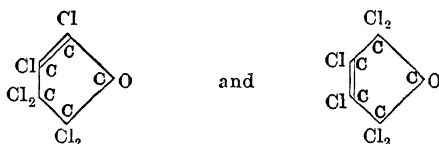
³ *l. c.* 28, 767; *Guthzeit*, *l. c.* 31, 2753.

liquid only slowly and with transformation into the other; on treatment with acid and shaking out with ether the enol-form is recovered. It may be added that the two formulae might be confirmed by the fact that the first compound should exist in two isomeric states, like fumaric and maleic acids:



while the second, containing an asymmetric carbon atom, should split into two optical antipodes.

As a second item towards the explanation of the behaviour of tautomeric compounds, Küster's¹ proof should be mentioned that a mixture in chemical equilibrium can actually be obtained by means of partial transformation. The body considered was hexachlorketopentane, $\text{C}_5\text{Cl}_6\text{O}$, which is obtainable in two isomers, distinguished as β - and γ -compounds, with the probable constitutional formulae:



Actually the β -compound is distinguished by forming with aniline in alcoholic solution a slightly soluble anilide, which is made use of to determine the proportions of the mixture.

On heating, each isomer suffers a transformation leading to a mixture in chemical equilibrium that shows all the characteristics of a tautomeric compound. The formation of this mixture was followed out at 210.5° . Measured amounts of β -pentane were heated for a measured time (t), and after sudden cooling the fraction (x) converted into

¹ *Zeitschr. f. Phys. Chem.* 18, 161.

γ -pentane determined. The following table contains the results:—

t (in hours)	x	$-\frac{1}{t} \log (1-2.591x)$
0	0	—
1	0.046	0.0551
3	0.114	0.0507
5	0.173	0.0516
6	0.206	0.0552
8	0.255	0.0566
12	0.304	0.0561
18	0.352	0.0588
22	0.387	—
23	0.386	—

The final quantity 0.386 of γ -pentane was practically the same as the 0.387 left on heating pure γ -pentane for sixteen hours at 210.5°, and the course of the reaction corresponds to the equation that may be expected in such a transformation:

$$\frac{dx}{dt} = k(1-x) - k_1x,$$

that is, two unimolecular processes going in opposite senses. In the final condition

$$\frac{dx}{dt} = 0, \text{ so that } k(1-x) = k_1x,$$

and since

$$x = 0.386, \quad k_1/k = 1.591,$$

so that

$$\frac{dx}{dt} = k(1-2.591x),$$

whence

$$-\frac{1}{t} \log (1-2.591x)$$

must be constant, as the third column of the above table shows.

It may be added that Walden observed the same state of equilibrium between two isomers in the spontaneous formation of racemates. Active bromosuccinic ethyl ester, e.g., gradually loses its activity by transformation into a mixture

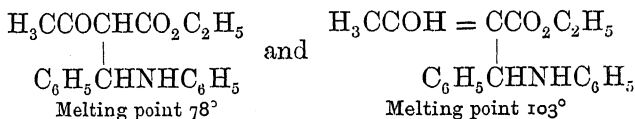
or compound of the optical isomers. The equation to the change is simplified on account of the similarity of the two opposing reactions, for

$$k = k_1,$$

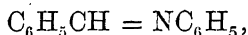
whence

$$\frac{dx}{dt} = k(1 - 2x).$$

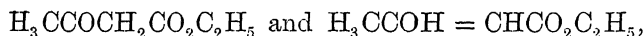
Finally the behaviour of aceto-acetic ether, apparently due to mutual transformation at ordinary temperatures, is most peculiar. The phenomenon has been accurately studied, especially by R. Schiff¹. He concluded, on the ground of the formation of the two isomers,



with the aid of benzaniline,



that aceto-acetic ether is a mixture of two isomers :



i. e. the keto- and enol-forms respectively. This view was confirmed by the fact that different preparations did not yield the isomeric benzaniline derivatives in the same proportion; one obtained from Kahlbaum giving the pure enol-form, another from Marquardt giving a mixture.

The measurements of Traube² point to the same conclusion, indicating a slow change in the density :

1.02443	15 minutes after distillation.
1.02467	20 hours later.

This went hand in hand with a change in the behaviour

¹ *Berl. Ber.* 31. 603.

² *I. c.* 29. 1715. See especially also Schaum, *l. c.* 31. 1564.

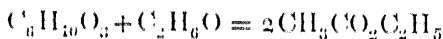
towards ferric chloride. The phenomenon was more striking in ethyl-alcoholic solution:

0.85966	after 10 minutes.
0.85963	" 1½ hours.
0.86072	" 20 "
0.86066	" 8 days.

In chloroform this was not observed:

1.42277	after 10 minutes.
1.42273	" 4 hours.

It is questionable, however, whether in alcoholic solution the process



did not occur.

Whilst, therefore, the latest information points to a tautomeric compound being a mixture in equilibrium of two isomers, it may be remarked¹ that such a phenomenon is only possible in a liquid or solution. In the solid state one or other compound must be the stable form, and the two can only coexist at the transition temperature. Liquid or dissolved, however, the condition of equilibrium is subject to gradual displacement with temperature, so that a mixture in equilibrium is possible over a considerable interval of temperature. In general, therefore, a solution of a pair of isomers near the transition point would behave as tautomeric.

Here we may add the remark that the phenomenon of tautomerism, like any other depending on atomic movements, must vanish at the absolute zero. This, however, is only in accordance with the known fact that tautomerism does not occur in the solid state. Long before the absolute zero all tautomeric compounds would become solid.

¹ Knorr, *Ber. Ber.* 30.2389.

III. MOLECULAR GROUPING

(Polymorphism)

WHILST polymerism is explained as difference in molecular weight, and isomerism in molecular structures, there remains a third difference in properties to account for, which is characterized by the fact that it disappears on conversion into the amorphous, i.e. liquid or gaseous state, consequently on fusion, evaporation, or solution. As example may be mentioned the rhombic and monosymmetric forms of sulphur, with regard to which it has lately been shown¹ that they form the same molecules S_8 on going into solution; along with these are to be placed the various crystallized modifications of ammonium nitrate, &c., studied by Lehmann; and finally the numerous polymorphic minerals, such as calcite and aragonite.

It is natural to refer these differences to variation in molecular grouping, since when the grouping ceases and the substance passes into the amorphous state, the differences vanish. For that reason polymorphism is most analogous to the physical change of state on melting or freezing; it is well known that a molecular orientation is then destroyed or created, whilst in a polymorphic transition one orientation appears at the expense of another. And so, if we are to distinguish between physical and chemical isomerism, it is convenient to regard polymorphism as physical isomerism, and polymerism and isomerism as chemical, since they in common rest on a change within

¹ Aronstein and Meihuizen (see p. 60).

the molecule. The word allotropy may then be retained for the phenomena of isomerism in the elements, whether they are to be characterized as polymerism, like ozone (O_3) and oxygen (O_2), or polymorphism, like rhombic and monosymmetric sulphur.

The general remark may be added that, as was explained earlier (p. 82), the phenomena of polymerism and isomerism are rare in the inorganic province, and the differences accompanying similarity of composition there met with are almost entirely to be referred to polymerism. It is remarkable that the tenacity with which organic compounds retain a molecular structure which is, nevertheless, not that of equilibrium, a property mostly wanting in inorganic compounds, is replaced by tenacious retention of molecular grouping. Two points of view are advantageous for complete treatment. First, we will bring forward the laws of transition in polymorphic substances. Secondly, we may discuss the details of molecular grouping.

§ I. LAWS REGULATING THE MUTUAL CONVERSION OF POLYMORPHIC SUBSTANCES.

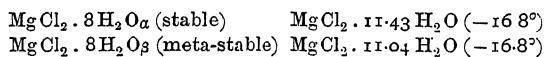
These laws may be deduced from the two facts that the polymorphic substances are solids of similar composition, and that on passing over into vapour, solution, or the fused state, the difference between the two modifications disappears.

We have, however, in the following discussion, to bear in mind the conditions of equilibrium, that mutual conversion of the two modifications, especially in the case of polymorphic minerals, such as calcite and aragonite, does not occur; we have, therefore, to deal, in one of the two cases, with a state of apparent equilibrium (Part I, p. 236) which is not destroyed even by contact with the other modification, and is not to be referred to an extremely slow transition. It is natural to associate this rigidity with the relatively great hardness of the minerals.

Let us now put together the chief results with regard to mutual conversion; these refer firstly to cases of polymorphism in which a conversion takes place slowly in one direction or the other, due to contact with the other modification. In these cases we may clearly describe one modification as stable, the other as meta-stable.

A. The Stable Modification must have the Smaller Vapour Pressure and the Smaller Solubility.

The necessity of this rule follows because only in this case would a change from the meta-stable to the stable phase necessarily occur by means of the vapour, or on contact with a solvent by means of it. If the reverse condition of solubility held, the transition would take place in the reverse direction on suitable application of a solvent; the direct conversion would then allow of a possible cyclic process that would be equivalent to a perpetual motion. A direct confirmation of the greater solubility of the meta-stable variety has been given in the case of magnesium-chloride octohydrate¹, of which the saturated solutions possess the following composition:—



B. The Stable Modification must have the Higher Melting Point.

In Fig. 25 the saturation pressure p of the two modifications I and II is represented as a function of the temperature, and I possessing the higher pressure is consequently the meta-stable phase. If now we draw a third curve, III, representing the vapour pressure of the liquid substance, the points of intersection, A and B, with I and II obviously represent the melting points of the two forms, and, as may be seen, A, the melting point of the meta-

¹ Van 't Hoff, Meyerhoffer, *Zeitschr. f. Phys. Chem.* 27. 87.

stable form, refers to the lower temperature. Thus, e.g., benzophenone in the stable form melts at 48° , in the meta-stable at 26° .

C. Possibility of a Transition Temperature.

As in all condensed systems, if a transition takes place between polymorphic modifications it must be carried out completely at one temperature. The direction in which it takes place may, however, depend on temperature, as may be seen from the vapour pressure curves. If the curves I and II for the two modifications show a point of intersection A (Fig. 26), then below the temperature T_A corresponding to it the modification to which II refers will be formed from the other: above that temperature the state of things is reversed, and consequently on passing that point

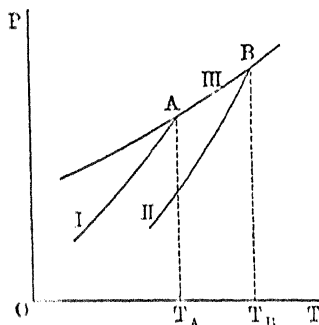


Fig. 25.

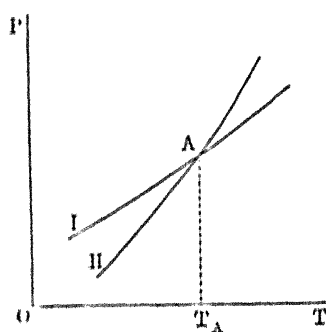


Fig. 26.

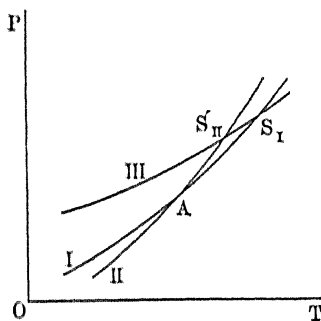


Fig. 27.

a total conversion takes place, as is the case with rhombic sulphur at 95.6° , when it is converted into monosymmetric. Lehmann has proposed to call phases such

as those of sulphur, for which there is a transition temperature, enantiotropic; the others, for which the reaction will go in one sense only, such as benzophenone, monotropic. The latter phenomenon may obviously result from the transition point lying above the melting points of both modifications; thus Fig. 27 represents enantiotropy, Fig. 25 monotropy; in each figure curves I and II refer to the vapour pressure of the two solid phases, III to that of the liquid.

D. When there is a Transition Temperature, the Modification stable at Low Temperatures is formed from the other with Evolution of Heat.

The relations of vapour pressure, as shown in Fig. 26, give this conclusion at once, with the aid of the second law, in the form

$$AVdP = q \frac{dT}{T}.$$

Here V is the increase of volume on evaporation, i.e. practically the volume of the vapour; at the transition point this is the same for the two modifications, since they have the same vapour pressure. Further, as the figure shows:

$$dP_{II} > dP_I,$$

where II is the modification stable at low temperatures; therefore

$$q_{II} > q_I \quad \text{or} \quad q_{II} - q_I = R$$

is positive.

But now, since q_{II} and q_I are the latent heats of evaporation of the stable and meta-stable forms respectively, $q_{II} - q_I$ is the heat evolved on formation of the former from the latter; consequently the form stable at low temperatures is produced from the other with evolution of heat.

This law is very well illustrated by the researches of

Bellati and Romanese on ammonium nitrate¹. This substance freezes at 168° in the regular system; becomes rhombohedral at 124°, with an evolution of 11.86 calories per kilogram; at 82.5° becomes rhombic, with an evolution of 5.33 calories; and at 31° rhombic with a different axial ratio, with evolution of 5.02 calories.

E. Polymorphic Modifications have a Constant Ratio of Solubilities, proportional to the Differential Coefficients of the Saturation Pressures, in Solvents which take up so little of the Substance, that the Laws of Dilute Solutions are applicable.

This relation follows from the equation (Part I, p. 36)

$$\frac{d \log C}{dT} = \frac{Q}{2T^2},$$

which unites the concentration of the solution or vapour with the heat Q absorbed when one kilogram-molecule is dissolved or evaporated (without doing external work).

For the two polymorphic bodies we have

$$\frac{d \log C_1}{dT} = \frac{Q_1}{2T^2}$$

and

$$\frac{d \log C_2}{dT} = \frac{Q_2}{2T^2},$$

whence

$$\frac{d \log (C_2/C_1)}{dT} = \frac{Q_2 - Q_1}{2T^2} = \frac{R}{2T^2},$$

where R is the heat of transition.

Integrated, this gives:

$$\int d \log \frac{C_2}{C_1} = \log \frac{C_2}{C_1} = \int \frac{R dT}{2T^2} + \text{const.}$$

The constant is given by the fact that at the transition

¹ Lehmann, *Molekularphysik*, p. 159.

temperature P the concentrations C_i , C_u are equal, so that

$$\log \frac{C_u}{C_i} = \int_T^P \frac{RdT}{2T^2}.$$

Here, however, the second term is a quantity independent of the solvent, depending only on the heat of transition R , and which, therefore, remains unaltered even if C_i , C_u refer to vapour, so that their ratio is that of the saturation pressures.

This law, which might easily be proved for, say, calcite and aragonite, or for the sulphur modifications, retains a certain applicability even to isomers more widely separated, which do not become identical on solution. Carnelley and Thomas¹ found for isomeric benzene derivatives (para- and meta-nitraniline) the following two empirical laws:—

1. Of isomeric compounds, that with the lower melting point has the greater solubility.

2. The ratio of solubilities is independent of the solvent.

The latter rule corresponds literally with our conclusion as applied to solutions. The former equally corresponds to the fact of higher vapour pressure shown above to accompany lower melting point and greater solubility.

As is to be expected, however, the rule thus found is not universal, since it does not apply to polymorphic bodies, and so Walker and Wood² found, e. g. for ortho-, meta-, and para-oxybenzoic acid in water and benzene, the following solubilities:—

	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>	<i>Ortho</i> <i>Meta</i>	<i>Meta</i> <i>Para</i>
Water . . .	0.264	1.337	0.765	0.197	1.75
Benzene . . .	0.97	0.0121	0.0052	80.2	2.33

§ 2. ACTUAL MOLECULAR ARRANGEMENTS.

The answer to the question as to molecular arrangement involves two essentially distinct problems, one with regard to the relative position of molecule and molecule, the other

¹ *Journ. Chem. Soc. Trans.* 1888, p. 782.

² *l. c.* 1898, p. 618.

as to the orientation of the molecule in its surroundings. Let us take as a definite example the oxide of magnesium, periclase (MgO), whose molecules are to be thought of in a determinate arrangement, belonging to the regular system. Then we may ask whether the line joining an atom of magnesium and one of oxygen is parallel to one of the axes of the regular system, or perhaps corresponds to the direction of an octahedral edge, &c.

The two problems are treated separately in what follows, as :

A. Relative position of molecule centres in the crystalline figure.

B. Orientation of the molecules in the crystal.

A. Relative Position of Molecule Centres in the Crystalline Figure.

1. *The Fundamental Law of Geometrical Crystallography*¹ (F. C. Neumann).

Observation shows that normally grown crystals have the form of polyhedra, whose flat bounding faces cut each other at definite angles, while the area of the faces depends on accidental circumstances. The crystalline form of a body is therefore determined by the angles, i. e. by the relative position of the faces by which it is bounded. With regard to this position, however, observation shows further that not every possibility is found, but that the form of

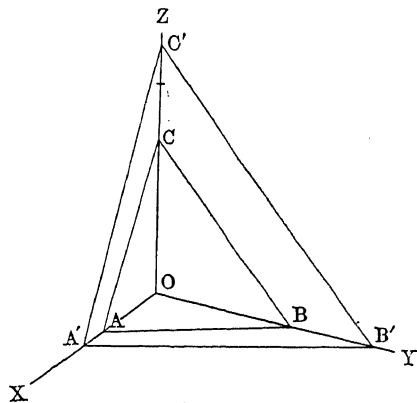


Fig. 28.

¹ Groth, *Physikalische Krystallographie*, 3rd ed. Leipzig, 1894.

a crystalline polyhedron follows the law usually known as the 'law of rational indices.'

This law states that any possible plane in a crystal can be determined by means of four planes, no three of which are parallel: in what way is best shown in Fig. 28 by drawing three of the planes about the point *o*, viz. *xoy*, *yoZ*, *zox*, and the fourth as *abc*. The position of a fifth plane, say *A'B'C'*, is conditioned by the fact that the ratio of the so-called indices

$$\frac{Ox'}{Ox} : \frac{Oy'}{Oy} : \frac{Oz'}{Oz}$$

can only be given by whole numbers, such as

$$m : n : p \text{—say } 2 : 3 : 5$$

or can only be rational.

In describing a crystalline form therefore, it is sufficient to give the angles made by a suitable group of four planes:

$$ZOY = \alpha, \quad ZOZ = \beta, \quad YOX = \gamma,$$

as axial angles, and the ratio

$$Ox : Oy : Oz = a : b : c$$

as axial distances, so that the whole crystal is defined by means of five elements.

2. *Attempt at Explanation of the Geometrical Law by Arrangement of Molecule Centres* (Frankenheim, Bravais).

A very simple conception, probable also on other grounds to be explained later, gives a plausible meaning to the above geometrical law. This consists in the assumption of a regular arrangement of the crystalline centres, such that they are alike and parallel throughout the crystal. As previously the position of four non-parallel planes sufficed for the entire structure, so here the position of four molecule centres, 1, 2, 3, 4 (Fig. 29), not lying on one plane. The axial angles then correspond to the angles between

a , b , and c , the axial distances to the lengths of a , b , and c . The condition that the arrangement round, e.g., point 4 should be similar and parallel to that round 1 is satisfied by choosing the point 5 in a direction and distance from 2 parallel and equal to b . In the same way 6, 7, and 8 are arrived at, and so an elementary parallelepiped completed. This may then be developed into a regular point system (Fig. 30) by extending the line a to an equal extent, to obtain a new point, and so on. Such an arrangement of molecule centres would reproduce the relations of a crystalline figure¹.

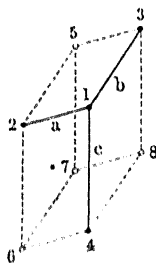


Fig. 29.

If, now, the bounding faces of the crystal are planes in which molecule centres are contained, they may pass either through 2, 3, 4 or through 1, 2, 3 or through 1, 2, 4 or through 1, 3, 4. With any other choice, such as 1, 5, 6, the law of rational indices obviously holds, since each index corresponds to a row of points starting from 1 with a definite number of steps between them.

3. Relations of Symmetry in Crystals.

Just as a crystal is not capable of assuming any form, so the relations of symmetry of these forms are restricted, and from the above fundamental law of geometrical crystallography Hessel and Gadolin deduced all the actually observed relations. We cannot give the deduction here in full², but it may be shown how the law of rational

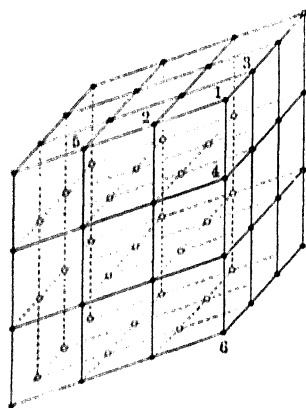


Fig. 30.

¹ Grah, *Theoretische Krystallographie*, 3rd ed., 1894, p. 248.

² Ibid., I. c. p. 311.

indices restricts the possibilities of symmetry. In the first place, by reference to Fig. 28 we see that there need be no symmetry at all, in which case we have the unsymmetric (triclinic) system.

One plane of symmetry may be present, but it is limited as to position; if e.g. it passes through zox , then the plane symmetrical to ABC would have rational indices with respect to ox and oz , but not in general with respect to oy ; it is therefore a subsidiary condition that oy should be perpendicular to the plane of xoz . These are the conditions for the non-symmetric system.

One axis of symmetry may be present, i.e. a line such that rotation about it through an angle less than 360° brings the crystal into a position identical with its original position. If e.g. the axis occupies the position oz (Fig. 28), the law of rational indices is satisfied when $xoy = 90^\circ$ and $oa = ob$; such axes are therefore, for the same reason, subjected to certain conditions; they can only be double, triple, quadruple, or sextuple, i.e. the form may recover its original position on rotation through 180° , 120° , 90° , or 60° , i.e. two, three, four, or six times in a circle. These are the conditions for the rhombic, trigonal, tetragonal, and hexagonal systems.

A third possibility is that the crystal on rotation comes into a position symmetrical to its original position; it is then said to have an axis and plane of compound symmetry.

In this way, taking into account the law of rational indices, thirty-two classes, exactly corresponding to the facts, are arrived at; and these are grouped in the seven crystalline systems:—

I. Triclinic system.

1. Holohedry. Example: calcium thiosulphate ($\text{CaS}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$).

2. Hemihedry: one double axis and one plane of compound symmetry at right angles to it. Example: *d*-monostrotrium tartrate ($\text{Sr}(\text{C}_4\text{H}_5\text{O}_6)_2 \cdot 2\text{H}_2\text{O}$).

II. Monoclinic system.

1. Hemimorphy: one double axis of symmetry. Example: cane sugar ($C_4H_{12}O_{11}$).
2. Hemihedry: one plane of symmetry. Example: potassium tetrathionate ($K_2S_4O_6$).
3. Holohedry: one plane of symmetry and a double axis of symmetry at right angles to it. Example: sulphur (S_8).

III. Rhombic system.

1. Hemihedry: three double axes of symmetry at right angles. Example: magnesium sulphate ($MgSO_4 \cdot 7H_2O$).
2. Hemimorphy: one double axis and two planes parallel to it and at right angles to one another. Example: struvite ($MgNH_4PO_4 \cdot 6H_2O$).
3. Holohedry: three planes of symmetry at right angles, and three double axes of symmetry at right angles. Example: sulphur (S_8).

IV. Tetragonal system (one quadruple axis).

1. Sphenoidal tetartohedry: one plane of compound symmetry at right angles to the quadruple axis. Not yet actually observed.
2. Hemimorphic hemihedry. Example: wulfenite ($PbMoO_4$).
3. Sphenoidal hemihedry. As in class 1; in addition, two double axes of symmetry at right angles to one another in the plane of compound symmetry, and two planes of symmetry which cut in the quadruple axis and bisect the angles of the double axes. Example: ($CuFeS_2$).
4. Trapezohedric hemihedry: four double axes in the plane at right angles to the quadruple axis. Example: nickel sulphate ($NiSO_4 \cdot 6H_2O$).
5. Pyramidal hemihedry: one plane of symmetry at right angles to the quadruple axis. Example: scheelite ($CaWO_4$).
6. Hemimorphic holohedry: four planes of symmetry cutting one another in the quadruple axis. Example: silver fluoride ($AgF \cdot H_2O$).
7. Holohedry: in addition to the above, four double

axes of symmetry and one plane of symmetry, all at right angles to the quadruple axis. Example: tinstone (SnO_2).

V. Trigonal system (triple axis of symmetry).

1. Hemimorphic tetartohedry. Example: sodium periodate ($\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$).

2. Rhombohedral tetartohedry: the triple axis is also the sextuple axis of compound symmetry. Example: diopase (CuH_2SiO_4).

3. Trapezohedral tetartohedry: three double axes in a plane at right angles to the triple axis. Example: quartz (SiO_2).

4. Bipyramidal tetartohedry: a plane of symmetry at right angles to the triple axis. Not yet actually observed.

5. Hemimorphic hemihedry: three planes of symmetry, cutting one another in the triple axis. Example: tourmaline.

6. Rhombohedral hemihedry: besides the foregoing, three double axes of symmetry in the plane at right angles to the triple axis. Example: corundum (Al_2O_3).

7. Bipyramidal hemihedry: like No. 5, but in addition a plane of symmetry and six double axes of symmetry, all at right angles to the triple axis. Not yet actually observed.

VI. Hexagonal system (sextuple axis of symmetry).

1. Hemimorphic hemihedry. Example: nepheline ($\text{Na}_3\text{Al}_3\text{Si}_3\text{O}_{34}$).

2. Trapezohedral hemihedry: six double axes in a plane at right angles to the sextuple axis. Example: antimonylbaric tartrate + potassium nitrate ($(\text{C}_4\text{H}_4\text{O}_6\text{SbO})_2\text{Ba} \cdot \text{KNO}_3$).

3. Pyramidal hemihedry: one plane of symmetry at right angles to the sextuple axis. Example: chlorapatite ($\text{Ca}_5\text{Cl}(\text{PO}_4)_3$).

4. Hexagonal hemimorphism: six planes of symmetry cutting one another in the sextuple axis. Example: silver iodide (AgI).

5. Holohedry: like No. 4, but in addition one plane of symmetry and six double axes of symmetry, all at right angles to the sextuple axis. Example: beryl ($\text{Al}_2\text{Be}_3(\text{SiO}_3)_6$).

VII. Cubical system.

1. Tetartohedry: three equal rectangular double axes of symmetry, and four equal triple axes equally inclined to the double axes. Example: sodium chlorate (NaClO_3).

2. Plagihedric hemihedry: three equal rectangular quadruple axes of symmetry, four triple axes as in the preceding, and six double axes bisecting the angles between the quadruple axes. Example: cuprite (Cu_2O).

3. Pentagonal hemihedry: as in No. 1, but in addition three planes of symmetry at right angles to the double axes. Example: pyrites (FeS_2).

4. Tetrahedric hemihedry: planes of symmetry as in No. 3, but in addition six planes which bisect the angles between the former planes.

5. Holohedry: three equal rectangular quadruple axes of symmetry, four triple and six double axes as before, in addition all the planes of symmetry of classes 3 and 4. Example: galena (PbS).

4. *Sohncke's Point Systems.*

The species of regular gratings in space arrived at by Bravais and Frankenheim, on the assumption of an equal and parallel arrangement throughout the crystal, satisfy the law of rational indices, but do not allow of obtaining all the thirty-two classes of forms described above; they lead indeed to seven systems, but only to fourteen classes¹.

In the year 1879 Sohncke² extended this conception by rejecting the restricting condition involved in it, that the arrangement round each molecule in the crystal is not only similar, but parallel. The latter is not necessary with regard to the actual observations on crystals; or rather it is definitely not always the case. The observation of Baumhauer on calcite, for example, is conclusive on this point. Place a prismatic cleavage block (Fig. 31) firmly

¹ Sohncke, *Pogg. Ann.* 1867, 132. 75.

² *Entwicklung einer Theorie der Krystalstruktur*, Leipzig.

with an obtuse edge horizontal (best by fitting it into a corresponding cut in a board), so that the long diagonal ce of the right end-face $cdef$ is also horizontal, put the blade of a knife at a at right angles to the upper edge, and press it gradually into the crystal; then

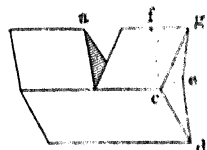


Fig. 31

the part of the crystal to the right of the knife will be deformed in such a way that when the knife reaches the middle edge it will have assumed exactly the form of an oppositely-placed half-rhombohedron. The part of the calcite occupying the new position is

quite homogeneous physically, but has its plane of cleavage parallel to ceg instead of ced as formerly.

Taking into account this possibility of an arrangement which is similar round each molecule, but not parallel, Sohncke arrived at 65 regular point systems (extended by Schönflies and Fedorow to 230) which in general consist of several congruent interlaced spatial 'gratings.' They fall, according to their symmetry, into seven systems, like the spatial gratings, and yield exactly the 32 classes of possible crystallographic forms given by the fundamental law of geometrical crystallography¹.

5. *The Fundamental Law of Physical Crystallography.*

If Sohncke's theory corresponds, on the one hand, to the geometrical relationships of crystals, it allows, on the other, an attempt at explanation of their physical behaviour. Symmetry of external form is referred to that of the internal structure, and explains at once why symmetry of physical properties coincides with that of the external form, which, it is well known, is the content of the fundamental law of physical crystallography.

Take, as example, the hardness of rock salt. This shows

¹ Groth, *Physikalische Krystallographie*, pp. 268, 277.

three equal minima in the direction of the axes (edges of the cube) and four equal maxima at right angles to the octahedral faces; the figure which represents the hardness in all directions round a point by radii proportional to it has the symmetry of the cube form, i.e. three planes of symmetry at right angles to one another, and six others which pass through the lines of intersection and bisect the angles between the first three planes.

6. *Molecular Compounds.*

A concluding remark may be appended here. The possibility of measuring molecular weights, due to the theory of solutions, leads to the conclusion that the molecules are usually of the smallest size that is in agreement with the chemical data. In crystals, too, so far as the theory of solid solutions (p. 70) has been applied, no higher molecular complexes seem to occur. By the side of this the fact appears somewhat surprising that in hydrates, e.g. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, molecules are found possessing a high degree of complexity. These seem, however, restricted to the solid state, and certainly highly complex liquid molecules have not been found to exist; on the contrary, everything points to such hydrates breaking down in solution. The interlaced spatial gratings of Sohneke's point systems allow a conception of such hydrates, according to which the different molecules would belong to different gratings. It is important for this view that some such hydrates can lose their water of crystallization without destruction of the crystalline form, although their internal physical properties are changed; they take up water again on being placed in their former conditions. Mallard¹ and Klein² observed this phenomenon with certain aqueous silicates, the zeoliths. Lately the same thing has been observed by

¹ *Bull. de la Soc. minéral. de France*, 5. 255.

² *Zeitschr. f. Kristallographie*, 9. 38.

Tammann¹ with platinum double cyanides, whose composition can vary between MgPtC_4N_4 6.25 and $6.8\text{H}_2\text{O}$ without loss of crystalline form.

B. Orientation of the Molecules in the Crystal.

1. *Relations between Symmetry in the Crystal and in the Molecule.*

Since the application of the methods for determining molecular weights to solids (p. 70) has made it highly probable that the solid state is not characterized by the condition of complex molecules, the way is open to bring the configuration of molecules, as already developed (p. 90), into relation with crystalline form, and especially with the arrangement of molecules in regular point systems (p. 141) which give a plausible molecular-mechanical explanation of that form.

We may first mention what, of such researches, refers to the relations of symmetry in the molecule and in the crystalline structure. The leading result is the necessary conclusion pointed out by Pasteur, that a whole made up of similar asymmetric molecules cannot possess symmetry. What in his time could not be sharply formulated has since the development of stereochemistry become immediately clear². Consider as unsymmetrical grouping such as one assumes on presence of an asymmetric carbon atom, e. g. in ammonium bimalate :



in which the four different atomic complexes or atoms, COOHCH_2 , H, OH, COONH_4 , are thought of as in tetrahedral arrangement round the carbon atom distinguished by underlining (Fig. 16, p. 105); a regular arrangement of

¹ Buxhoevden and Tammann, *Zeitschr. f. anorg. Chem.* 1897, p. 319; *Wied. Ann.* 1897, p. 16. See also Rinne, *Neues Jahrb. Mineral.* 1899, L. p. 1; Joannis, *Comptes Rend.* 109. 965, 110. 238.

² Becke, *Min. u. petrogr. Mitteilungen von Tschermak*, 10. 414, 12. 256.

such figures can never lead to a symmetrical whole. So the crystalline form too of this salt is a rhombic form made unsymmetrical by the presence of the semi-pyramids, in front, above on the left, below on the right; behind, above on the right, below on the left. Though the external form in such cases does not always show the absence of internal symmetry, other indications of the asymmetry are present as erosion figures¹.

If the molecule is symmetrical, still the arrangement in the crystal may lead to an unsymmetrical whole, as is the case, e.g., with quartz (SiO_2), whose molecular constitution is symmetrical, as appears from its triatomicity, as well as from its inactivity in the fused state. Just for this case, Sohneke² worked out a crystalline structure that gives an account of the enantiomorphic and therefore asymmetric reflected image forms of quartz, and the opposite and equal optical activity associated with them. Assume first three spatial gratings,

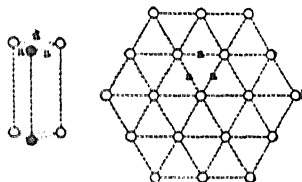


Fig. 32.

in which the particles are arranged according to the trigonal prism (Fig. 32), interlaced as in Fig. 33, in which they are projected on the base of the prism; point 1 requires a rotation of 120° about an axis passing normally through the centre of the triangle 1, 2, 3, and a displacement along the latter, to come into the position of point 2; the latter, a similar screw movement, to become 3; finally, a repetition of the movement gives a fourth point, whose projection, however, coincides with that of 1. If then we draw a circle through the projections

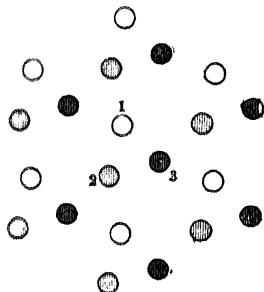


Fig. 33.

¹ See the discussion Trube, Walden, *Berl. Ber.* 29. 1692, 2447; 30. 98, 288.

² Groth, *Physik. Kristallographie*, 1894, p. 262.

1, 2, 3, and on it, as base, erect a cylinder at right angles to the plane of projection, it is plain that the particles will lie on its surface in spiral order, which is right-handed (like a corkscrew) when 3 is twice as far above the plane of 1 as 2 is, but left-handed when 3 is twice as far below that plane as 2 is. The spirals show these opposite senses whether looked at from above or below; such a right- and left-handed spiral can in no way be made to coincide, for one is the reflected image of the other, and they are therefore called enantiomorphic.

Finally, symmetry, if it exists in the molecule, may be raised by the crystal¹. Two tetragonal pyramids, placed symmetrically on the same base, if they have the form of half octahedra, become an octahedron and so possess the symmetry of the regular system with nine planes of symmetry, while the individual molecules have only four.

The symmetry present in the molecule may therefore be either raised or lowered by arrangement in the crystal; for a greater number of compounds in which the opposing influences, tending to raise and lower the symmetry, partly neutralize, the remark of Buys-Ballot holds that the simpler the composition, and consequently greater the symmetry of the molecule, the greater the symmetry of the crystal. The following table² allows of forming an opinion on this point:—

Composition	Elements	Diatonic	Triatonic	Tetratonic
No. of bodies	40	67	63	20
Regular	50%	68½%	42%	5%
Hexagonal	35 "	19½ "	11 "	35 "
Tetragonal	5 "	4½ "	19 "	5 "
Rhombic	5 "	3 "	23½ "	50 "
Monoclinic	5 "	4½ "	3 "	5 "
Triclinic	0 "	0 "	1½ "	0 "
Mean Symmetry	8.4	7.9	6.2	4.7

As an expression of the entire condition, we have chosen the mean symmetry, obtained by multiplying each per-

¹ See, among others, Barlow, *Zeitschr. f. Kryst.* 1898.

² *Zeitschr. f. Phys. Chem.* 14. 1, 548.

tage by the number of planes of symmetry corresponding, viz. 9, 7, 5, 3, 1, 0, and dividing the sum of these products by 100. Like all statistical relations this has the disadvantage that the application to particular cases often fails.

2. *Influence of Changes in the Molecule on the Crystalline Form.*

In the preceding, attention was paid to the direct relation between symmetry or the want of it in the molecule and the crystal. A second line of research is that of the influence which changes in the molecule exert on corresponding changes of form. Let us take first the smallest changes which show themselves in the orientation or relative position in the molecule, as polymorphism, while the molecule as a whole remains the same. Here we have clearly a point of departure in judging of the relations between molecular configuration and crystalline structure, since the same configuration is associated with two different figures. The observations collected on this subject are, however, so far of a purely empirical character, and amount to no more than the important remark that, when the crystalline form of a polymorphic substance changes, there is often a striking equality in the angular and axial relations to be noted¹. Let us consider examples.

Potassium nitrate, potassium sulphate, and calcium carbonate, which can all take hexagonal form, i.e. with the angle 60° , show in their possible rhombic forms prism angles not very different from 60° —actually $60^\circ 36'$, $59^\circ 36'$, and $63^\circ 44'$ in the three cases.

Basic copper nitrate, $\text{Cu}_2(\text{OH})_2\text{NO}_3$, which is found in rhombic form with the axial ratio

$$a : b : c = 0.9217 : 1 : 1.1562,$$

is converted into a monoclinic form with almost the same ratio,

$$a : b : c = 0.919 : 1 : 1.1402,$$

¹ Arzruni's collection in Graham-Otto, 1893, 74.

and an axial angle not very far from 90° :

$$\beta = 94^\circ 33'.$$

Finally the silicate, $\text{H}_2\text{Mg}_{10}\text{Si}_8\text{O}_{34}\text{F}_4$, is found as humite (rhombic):

$$a : b : c = 1.0803 : 1 : 4.4013,$$

as chondrodite (monoclinic):

$$a : b : c = 1.0803 : 1 : 3.1438 \quad \beta = 90^\circ,$$

and as clinohumite (monoclinic):

$$a : b : c = 1.0803 : 1 : 5.6588 \quad \beta = 90^\circ.$$

This equality of form on change of structure would perhaps come out more strikingly if the comparison of angles and lengths were made, not at the ordinary temperature, but at the transition point, since then the two forms have just the same stability, a fact which may be due to mechanical causes. In any case it is to be remarked that this relation between the two forms is associated with the possibility of a transition without upsetting the internal connexions of the substance. Thus, e.g., boracite passes at 266° into the regular form without any loss of transparency, but only with a sudden change of optical properties, becoming singly refracting.

Isomeric change constitutes a deeper modification in the molecule. Accordingly, the accompanying change—mostly complete—in the symmetry of the molecule corresponds to a complete change in molecular structure, without any relations that have so far been traced. In one case, however, the circumstances are different, viz. in that of stereo-isomers with an asymmetric carbon atom. The two isomers here present, as we have seen, a difference of configuration shown in Figs. 16 and 17 (p. 105), and known as enantiomorphic. A completely analogous enantiomorphic difference is found in the crystalline form, as is shown in Fig. 18 and 19 (p. 106), for the oppositely active ammonium bimalates.

On passage from the active compounds to the racemate, in which the enantiomorphic molecules unite, the enantiomorphism of crystalline structure is also destroyed, as a rule. In the cases hitherto studied the following axial ratios have been found:—

Potassium bitartrate, $\text{KC}_4\text{H}_5\text{O}_6$,

Rhombic $a:b:c = 0.7168:1:0.7373$

Potassium biracemate, $(\text{KC}_4\text{H}_5\text{O}_6)_2$,

Triclinic $a:b:c = 0.7053:1:0.7252$

$\alpha = 88^\circ 36'$ $\beta = 102^\circ 22'$ $\gamma = 87^\circ 16'$,

so that at any rate two axial angles are not far from 90° .

If we have here a striking relation between the configuration of the molecule and crystalline structure, it becomes much more so on considering the phenomena of isomorphism, which Mitscherlich first put in the right light. That two bodies like potassium-magnesium sulphate and rubidium-cadmium sulphate, despite their entirely different composition:

19.4 % Potassium	29.2 % Rubidium
6 " Magnesium	19.3 " Cadmium
15.9 " Sulphur	11 " Sulphur
55.7 " Oxygen	38.5 " Oxygen
1 " Hydrogen	2 " Hydrogen

should possess the same monoclinic crystalline form, which, moreover, indicates so close a similarity in internal structure that they form completely homogeneous mixed crystals in which one compound has replaced the other, is a most conclusive proof that the molecular-mechanical conception of the compounds, attributing to them the analogous formulae,



comes very near to the facts if only schematically.

It is on this ground of isomorphism that considerations may be developed allowing of a deeper insight into the structural relations in crystals.

In the first place we must consider the investigation started by Groth on so-called morphotropy, i.e. small changes of form which are produced by change of composi-

tion despite prevailing isomorphism. The following measurements of Topsøe furnish an example; all the compounds are hexagonal :—

$NR_4Cl \cdot 5HgCl_2$	$a : c$
$R_4 = (CH_3)_3H$	1 : 1.1075
$R_4 = (CH_3)_4$	1 : 1.1002
$R_4 = (CH_3)_2(C_2H_5)_2$	1 : 1.0855
$R_4 = (C_2H_5)_4$	1 : 1.0512
$R_4 = (C_3H_7)_3H$	1 : 1.029
$R_4 = (C_2H_5)_2H_2$	1 : 1.025
$R_4 = (C_2H_5)_3H$	1 : 1.017
$R_4 = (C_2H_5)_3H_3$	1 : 0.9955

Deeper changes are observed in the following cases ¹:—

$PtCl_4 \cdot 2NR_4Cl$	System	Axial ratio	β
$R_4 = (CH_3)_4$	regular	—	—
$R_4 = (CH_3)_3C_2H_5$	„	—	—
$R_4 = (CH_3)_2(C_2H_5)_2$	tetragonal	1 : 1.0875	—
$R_4 = (CH_3)(C_2H_5)_3$	„	1 : 1.0108	—
$R_4 = (C_2H_5)_4$	monoclinic	0.9875 : 1 : 0.9348	90° 46'

Here the influence affecting the form of the crystal has changed its system, yet without much alteration in the axial ratio or angle. Here plainly we have to do with di- or tri-morphism, and the morphotropic action has modified the transition temperatures, so that, e.g., with the tetramethyl derivative at the ordinary temperature the regular form, but with the dimethyl-diethyl derivative the tetragonal form, is the more stable.

The new researches of Tutton ² and Muthmann ³ carry us still further in the direction of an insight into the position of the molecules in a crystal. From the latter work we may take some results relating to the tetragonal phosphates and arsenates, whose isomorphism was observed by Mitscherlich :

Substance	Molecular volumes	$a : c$	a	c
KH_2PO_4	58.246	1 : 0.6640	1	0.664
KH_2AsO_4	62.822	1 : 0.6633	1.026	0.683
$NH_4H_2PO_4$	64.170	1 : 0.7124	1.009	0.719
$NH_4H_2AsO_4$	68.842	1 : 0.7096	1.031	0.732

¹ Arzruni, l. c. 233.

² Journ. Chem. Soc. Trans. 1893. 337, 1894. 628, 1896. 344.

³ Zeitschr. f. Krystallographie, 1894.

We see from these data, first, that in isomorphic compounds unequal difference in composition gives an equal difference in volume, for the molecular volume (molecular weight divided by the density) gives:

for As—P in the potassium salt . . .	4.576
„ ammonium „ . . .	4.672
and	
for NH ₄ —K in the phosphate . . .	5.924
„ arsenate . . .	6.020.

Next, however, and this is the chief result, the axial ratio remains almost unaltered on replacement of phosphorus by arsenic, but changes by a considerable amount on replacement of potassium by ammonium. Let us calculate, in order to express this behaviour more precisely, the dimensions of the fundamental parallelopiped, keeping for potassium phosphate the values

$$a = b = 1, \quad c = 0.664.$$

The volume is then $\frac{1}{2} a^2 c$, and so

$$a^2 c \left(= 0.664 \right) : a_1^2 c_1 = 58.246 : 62.822,$$

where a_1, c_1 refer to the fundamental parallelopiped of potassium arsenate. But since

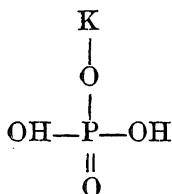
$$a_1 : c_1 = 1 : 0.6633,$$

we get

$$a_1 = 1.026, \quad c_1 = 0.683.$$

The corresponding values for the other salts are given in the fourth and fifth columns of the table. It follows that on replacement of potassium by ammonium, there is produced essentially only an increase in the height c of the fundamental parallelopiped amounting to 0.055 and 0.049 respectively; while a is practically unaltered, or only by the amounts 0.009 and 0.005 respectively. On the other hand, replacement of phosphorus by arsenic not only

increases c by 0.019 or 0.013, but also a by 0.026 or 0.022. It is then natural to assume that with the configuration



the line passing through $\text{K}-\text{O}-\text{P}=\text{O}$ gives the direction of the principal axis c , so that the enlargement due to substitution of NH_4 for K only lengthens the principal axis, whereas that due to the substitution of As for P produces an expansion in all directions.

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